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CHEMICAL SCIENCES

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NUMBER 2

ON THE MECHANISM OF OXIDATION OF *trans*-DECAHYDRONAPHTHALENE AT 100° C.¹

BY D. S. McARTHUR AND E. A. SMITH

Abstract

The mechanism of oxidation of the *trans*-isomer of decahydronaphthalene (*trans*-decalin) by gaseous oxygen at 100° C. has been studied. The rate of retention of oxygen by decalin and the rates of formation of three volatile oxidation products were measured over the first 100 to 200 hr. of the oxidation reaction. The rate of retention of oxygen has been found to be independent of the oxygen concentration in the oxidizing gases but to depend on decalin concentration to the three-halves power. The rates of formation of the volatile oxidation products are also independent of oxygen concentration but are proportional to the decalin concentration. The activation energies of each of the reactions were determined. An initiating reaction forming carbon monoxide and hydrogen has been postulated based on the ratio of the rates of formation of the volatile compounds in the inhibited period of oxidation. Some data on the mechanism of the oxidation reaction in the accelerated period have also been obtained.

Introduction

The mechanism of oxidation of decalin (decahydronaphthalene) by gaseous oxygen at 100° C. has never been elucidated. Balsbaugh and Oncley (1) oxidized decalin at 75° C. and found that peroxides were formed almost exclusively in the initial period. Larsen *et al.* (15) oxidized decalin at 110° C. and determined the amount of saponifiable material, acids, etc., among the oxidation products. Ivanov and Savinova (10) oxidized decalin at 70° C. under the influence of ultraviolet light and found that the hydroperoxide was formed. However, no attempt was made by these authors to determine the actual mechanism of the oxidation reaction.

In this work the *trans*-isomer of decalin was oxidized at 100° C. The rate of oxygen uptake by the decalin and the rates of formation of three volatile oxidation products were followed as the oxidation progressed. It was possible to determine the effect of temperature, the effect of decalin concentration, and the effect of oxygen concentration in the oxidizing gases on the oxidation reaction. The data obtained give some insight into the mechanism of the oxidation reaction in the initial stages. Some evidence of the type of mechanism accounting for oxygen uptake in the accelerated period was also obtained from a partial analysis of the oxidation products formed in the decalin.

¹ Manuscript received June 24, 1948.

Contribution from the Department of Chemical Engineering, University of Toronto, Toronto, Ont.

Experimental

Epilome

Samples of 100 ml. of decalin were held at 100° C. and subjected to oxidation by the passage of a continuous stream of oxygen in a closed circuit. The volatile oxidation products were absorbed from the oxygen stream and determined by periodic weighing of the absorbers. The total oxygen flow into the closed circuit was measured and recorded automatically. The oxygen absorbed and retained by the decalin was determined from the difference between the total oxygen consumed in the circuit, as recorded automatically, and the oxygen collected with the volatile oxidation products as determined from the absorbed weights.

The effect of temperature on the reaction was determined by making oxidation runs at temperatures ranging from 80° to 120° C. The effect of decalin concentration was determined by oxidizing solutions of decalin in silicone fluid, and the effect of oxygen concentration was determined by oxidizing the decalin with oxygen diluted with nitrogen.

The Oxidation Apparatus

The oxidation apparatus used was patterned after that used by Fenske *et al.* (6). It consisted essentially of two parts, a circulating system in which oxygen was circulated continuously through the decalin sample by means of a glass-mercury pump (12), and an inlet line that maintained a constant, positive oxygen pressure (5 mm. mercury over atmospheric) on the circulating system and that measured and recorded the amount of oxygen flowing into the circulating system.

The pump drew oxygen from a reservoir and forced it through a buffer and flowmeter into the decalin sample. The oxygen stream bubbled through the sample and passed on, carrying with it the volatile oxidation products formed and a little vaporized decalin. The stream passed through a Graham condenser (which condensed out part of the decalin vapor) and through water and carbon dioxide absorbers where water formed by the oxidation reaction was removed. (It was found that no carbon dioxide was formed.) The oxygen stream then passed into a cold trap held at -70° to -80° C. where the remainder of the decalin vapor in the oxygen stream was trapped out. Any compounds sufficiently volatile to pass through the cold trap were ignited in a combustion furnace and the water and carbon dioxide formed were absorbed before the oxygen returned to the reservoir for recirculation. The hydrogen and carbon-bearing compounds ignited in the furnace were called "volatile hydrogen" and "volatile carbon" compounds respectively.

As oxygen was consumed in the circulating system, more passed in through the inlet line. The amount passing in was measured and recorded automatically by a wetmeter and oxygen-recorder system so that a continuous record of the oxygen consumed in the circulating system was kept as the oxidation run progressed.

That portion of the total oxygen consumed that was combined with the volatile oxidation products was determined by periodic weighings of the absorbers. Two parallel sets of absorbers were supplied so that the oxidation run did not have to be interrupted. Analysis of the small amounts of decalin (0 to 3 ml. in 100 hr.) trapped out from the oxygen stream indicated that no oxygenated compounds were removed with the decalin vapor. The portion of the total oxygen consumed that was absorbed and retained by the decalin could therefore be determined by difference.

It was found convenient to base all calculations on the moles of oxygen reacted or combined per liter of liquid sample being oxidized, and the results are reported in this form. Reaction rates are reported in moles of oxygen reacted per liter of sample per hour.

Chemicals

The *trans*-isomer or decahydronaphthalene (*trans*-decalin) was used in this work. It was obtained from commercial decalin. The decalin was first thoroughly acid-treated to remove aromatic and unsaturated compounds, shaken with ferrous sulphate to remove peroxides and dried over sodium hydroxide. The *trans*-isomer was then separated from the mixture by slow distillation at 10 to 12 mm. pressure through a Stedman column. The properties of the resultant product checked with those reported in the literature for *trans*-decalin.

The silicone fluid that was used as a diluent for the decalin was silicone fluid DC-550 as supplied by Fiberglas Canada Ltd. It absorbs oxygen at a low linear rate and forms water also at a low linear rate. However, since the rates are small compared to that for decalin, corrections could readily be made. It was found to be chemically inert in its effect on the rate of oxygen retention in decalin and on the rate of formation of water in the oxidation reaction.

Results

Under the conditions described, in which oxygen was bubbled through the decalin at 100° C. and recirculated after absorption of the water and removal of the volatile hydrogen and carbon compounds, it was found that about 81% of the total oxygen consumed in the circuit during the first 100 hr. is absorbed and retained by the decalin. Some preliminary work on the oxidized decalin indicated that this oxygen is divided with about half of it in the form of peroxides and a large part of the remainder in the form of hydroxy compounds and a small part (1 to 2%) in the form of an insoluble (in decalin) acid, 1-cyclohexene-1,2-dicarboxylic acid. About 13% of the total oxygen consumed reacts with the decalin to form water, which passes out of the reaction chamber with the oxygen stream as water vapor and is absorbed. The remainder of the oxygen consumed (about 6%) is combined with the volatile hydrogen and carbon compounds after their combustion to form water and carbon dioxide. The effects of temperature, decalin concentration, and oxygen concentration on these reactions are discussed in the following sections.

(a) *The Oxidation Reaction at 100° C.*

Each of the four reactions progressing simultaneously during the oxidation were studied:

- (1) The reaction by which oxygen was absorbed and retained in the decalin,
- (2) The reaction by which water was formed as a volatile oxidation product,
- (3) The reaction forming volatile carbon compounds, and
- (4) The reaction forming volatile hydrogen.

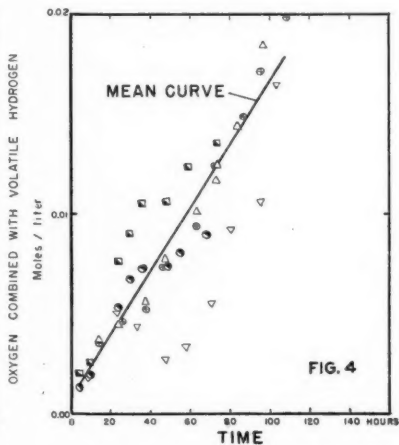
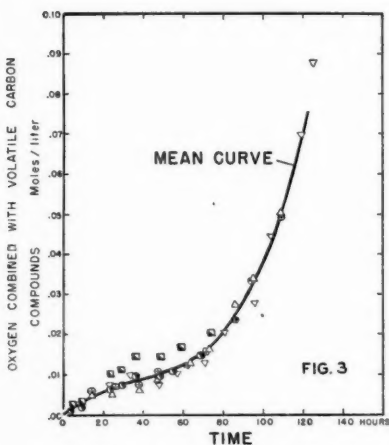
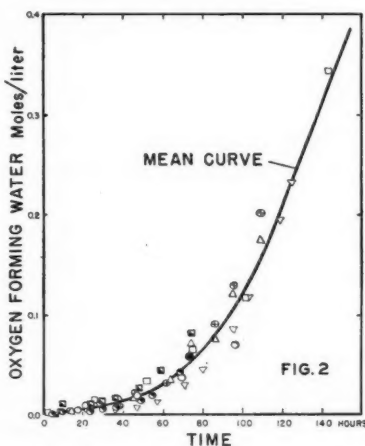
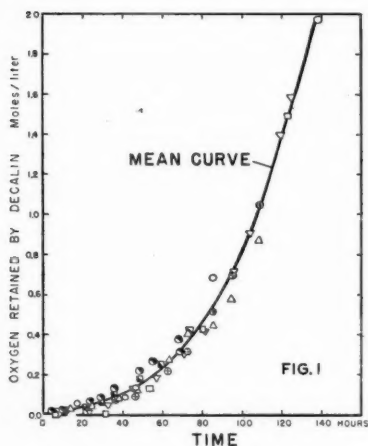


FIG. 1. Oxygen retained by decalin with time. Each set of symbols represents a separate test oxidation run.

FIG. 2. Oxygen combined to form water.

FIG. 3. Oxygen combined with volatile carbon compounds.

FIG. 4. Oxygen combined with volatile hydrogen.

The oxygen reacted or combined in each reaction is shown plotted against time in Figs. 1, 2, 3 and 4. It was found that no carbon dioxide is formed as an oxidation product during the first 100 hr. of the oxidation reaction. Fig. 1 shows that the decalin absorbs oxygen slowly at first with a gradual acceleration in the rate of absorption. A constant rate of about 360×10^{-4} mole of oxygen per liter per hr. is reached at 120 hr. as shown in Table I.

TABLE I
DATA ON THE OXIDATION REACTION AT 100° C.

Reaction	Reaction rates, moles O ₂ /liter/hr. $\times 10^4$		Activation energy, kcal./mole		Effect of decalin concentration [D] on reaction rate		Effect of oxygen concentration on reaction rate	
	Initial	Accel- erated	Initial	Accel- erated	Initial	Accel- erated	Initial	Accel- erated
Oxygen retention	—	361.3	23.0	23.0	None	$15.7[D]^{\frac{3}{2}}$	None	None
Formation of water	3.22	51.2	5.6	7.6	None	$8.20[D]$	None	None
Formation of volatile carbon compounds	2.09	25.0	10.2	20.7	$1.44[D]$	$2.58[D]$	None	None
Formation of volatile hydrogen	1.58	—	7.0	—	$0.53[D]$	—	None	—

The exact value for the initial rate of oxygen retention could not be determined.

Fig. 2 shows the absorption of oxygen by the water-forming reaction with time. The rate of water formation was found to be relatively constant at 3.2×10^{-4} mole oxygen per liter per hr. for 30 to 40 hr. followed by gradual acceleration to a steady-state rate of 51.2×10^{-4} mole oxygen per liter per hr. at about 120 hr. as shown in Table I.

Fig. 3 shows the oxygen combined with volatile carbon compounds plotted against time. The rate of formation of volatile carbon compounds is relatively constant over the first 60 hr. of oxidation at 2.1×10^{-4} mole oxygen per liter per hr. but then accelerates to about 25.0×10^{-4} mole oxygen per liter per hr.

Fig. 4 shows the formation of volatile hydrogen in terms of the oxygen combined with it to form water. The rate of formation is constant at 1.6×10^{-4} mole oxygen per liter per hr. throughout the entire period studied.

The idealized changes in the reaction rates with time as determined from the slope of the oxygen-reacted versus time curves are shown in Fig. 5.

(b) *The Effect of Temperature on the Oxidation Reaction*

The activation energy of each of the reactions was determined in both the initial and the accelerated period and these results are also shown in Table I.

In determining the activation energy the decalin concentration was assumed to be constant (pure decalin) throughout the run since only a small proportion of the decalin is oxidized during the initial oxidation period studied. The

oxygen concentration in the oxidizing medium was also held constant at 100% oxygen for these tests. The rate equation can therefore be simplified from:

$$\text{Rate} = K[\text{O}_2]^\alpha[\text{D}]^\beta$$

where

$[\text{O}_2]$ = oxygen concentration (constant),

$[\text{D}]$ = decalin concentration (constant),

α and β are constants

to

$$\text{Rate} = K \times \text{constant}$$

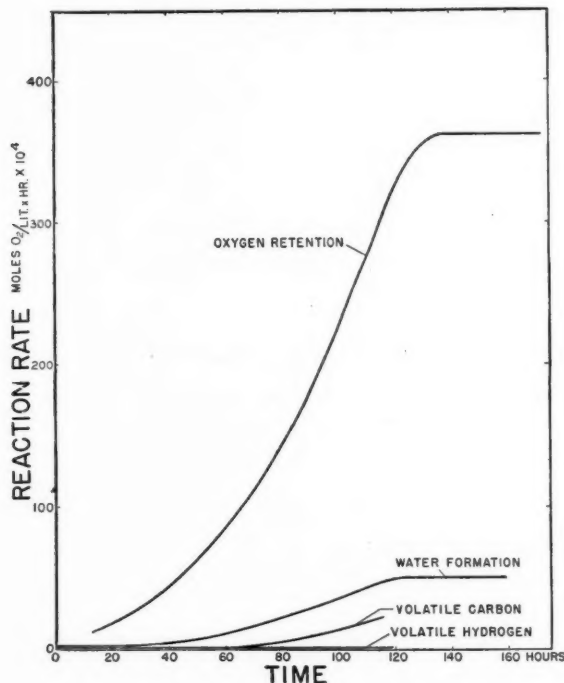


FIG. 5. The change in reaction rates with time.

The activation energy was determined from the slope of the plot of $\ln(K \times \text{constant})$ against $1/T$, where T is the absolute temperature.

In the case of the oxygen-retention reaction the reaction rates in the inhibited period were assumed to be inversely proportional to the length of the inhibited period as determined by projecting the accelerated absorption curve back to the time scale. In all other cases the reaction rates were determined directly from the slope of the oxygen reacted vs. time curves.

The results suggest that the same reaction accounts for oxygen retention in the decalin in both the initial and the accelerated period since the activation

energies in both cases are the same, 23.0 kcal. per mole. Water formation is by a reaction having a low activation energy (5 to 8 kcal. per mole) in both periods. Volatile carbon compounds are formed by a reaction having an activation energy of 10.2 kcal. per mole in the initial period (first 60 hr.) and by a reaction having an activation energy of 20.7 kcal. per mole in the accelerated period. Volatile hydrogen formation is by a reaction having a low activation energy (about 7.0 kcal. per mole) throughout the period studied.

(c) *The Effect of Decalin Concentration*

The effect of decalin concentration on the oxidation reaction was determined by making oxidation runs with varying proportions of decalin dissolved in the chemically inert silicone fluid.

The results obtained are also shown in Table I. There is no measurable effect of decalin concentration on the oxygen-retention reaction nor on the water-forming reaction in the initial stages. The oxygen-retention reaction however is quite sensitive to decalin concentration in the accelerated period, the rate being proportional to decalin concentration to the three-halves power as shown. All the other reaction rates are proportional to decalin concentration and differ only in the proportionality factors.

The silicone fluid catalyzes the initial rates of formation of volatile carbon compounds and volatile hydrogen. Two per cent silicone in decalin is sufficient to increase the rate of formation of volatile carbon compounds to 3.5 times the rate in pure decalin and to increase the rate of formation of volatile hydrogen to twice the rate in pure decalin.

(d) *Effect of Oxygen Concentration*

The oxidation reaction at 100° C. is completely independent of the oxygen concentration in the oxidizing mixture. An oxidation run was made in which the oxygen concentration in nitrogen was allowed to decrease from 50% to less than 1% as the run progressed. The system was then swept out with an oxygen-nitrogen mixture containing 80% oxygen and the run continued. In spite of the wide fluctuations in oxygen concentration, the experimental points obtained fell within the experimental error on the oxidation curves obtained with 100% oxygen. It was also observed that the reaction is independent of the rate at which the oxidizing gases are pumped through the system, provided the rate is in excess of some undetermined minimum.

(e) *Oxidation Products Formed in the Decalin*

In oxidation runs at 100° C. where more than 0.1 mole of oxygen is retained per liter of decalin, a small amount of a white crystalline precipitate settles out after the decalin has stood for a day or more at room temperature. Some roughly quantitative determinations indicated that it is formed in an approximately linear manner with time and at a very low rate, about 100 mgm. being

formed in a 100 ml. sample of decalin after 100 hr. of oxidation. The precipitate can be recrystallized from benzene, forming colorless, needlelike crystals that have been identified as 1-cyclohexene-1,2-dicarboxylic acid.

Some preliminary work was done using the method developed by Larsen (14) to determine the proportion of the total oxygen retained by the decalin which is in the form of acids, alcohols and/or hydroperoxides* ("Grignard added" oxygen). It was found as shown in Fig. 6 that there is a constant ratio between the oxygen found in the two classifications as the run progresses. Seventy-five per cent of the oxygen goes to form compounds of the "Grignard evolved" type and 25% goes to form compounds of the "Grignard added" type during the period studied.

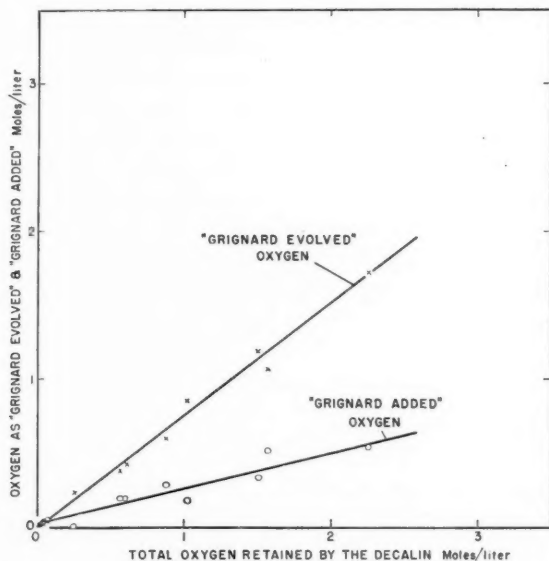


FIG. 6. Total oxygen retained by the decalin going to form "Grignard evolved" and "Grignard added" oxygen.

From quantitative tests on decalin samples drawn during the oxidation runs it was found that no carbonyl compounds are formed until 0.3 to 0.4 mole of oxygen per liter has been absorbed.

In oxidation runs where 0.8 to 1.0 mole of oxygen per liter is retained by the decalin, a viscous yellow liquid settles out. It is soluble in alcohol, acetone, acetic acid, ethyl acetate, ethyl ether, and benzene; partially soluble in decalin and carbon tetrachloride; insoluble in water, in dilute hydrochloric acid, and in dilute caustic (forming a white precipitate). It darkens with

* Hydroperoxides add one mole of Grignard and evolve one mole of methane, thus consuming two moles of Grignard reagent for each mole of the hydroperoxide.

cold concentrated sulphuric acid; reacts violently with acetyl chloride; shows no sign of unsaturation with bromine, and gives a negative test for carbonyl groups. The liquid darkens when boiled between 150° to 200° C. Analysis with Grignard reagent indicated that it contains oxygen of the "Grignard evolved" type (alcohols, acids). Elementary analysis indicated: C, 67.5; H, 9.36; O, 23.16%. It was not identified, but its chemical properties suggest that it consists largely of saturated hydroxy compounds.

Since no carbonyl compounds are present in the initial reaction stages, and from a comparison with the work of other authors (7, 8, 9, 17, 18) it seems likely that the major portion of the "Grignard added" oxygen is actually due to the presence of hydroperoxide. It follows that an equivalent amount of the "Grignard evolved" oxygen is also due to the hydroperoxide, so that approximately 50% of the oxygen retained by the decalin is present as the hydroperoxide. The saturated hydroxy compounds observed to separate out from the decalin in long oxidation runs indicate that a large part of the oxygen is also in this form.

Discussion

(a) *Initial Period of Oxidation*

As far as could be ascertained, the reaction by which oxygen is absorbed and retained by the decalin accelerates smoothly from the beginning of the oxidation, reaching a maximum steady rate of oxygen retention at 120 hr. The formation of the volatile compounds however occurs at a constant rate for the first 30 to 40 hours of the oxidation reaction. This suggests that the reaction forming the volatile compounds is an initiating reaction progressing at a constant rate and supplying radicals of a chain-initiating type which account for the smoothly accelerating rate of oxygen uptake by the decalin. After 30 to 40 hr. the formation of volatile products as a side reaction of the main oxygen-uptake reaction would account for the acceleration in the rate of formation of water and volatile carbon compounds in the later reaction.

The ratio of the rates of formation of the three volatile oxidation products during the initial 30 to 40 hr. is such that for each three molecules of water formed there are three atoms of volatile hydrogen and one atom of volatile carbon collected. The fact that the rate of formation of volatile carbon accelerates at 60 hr. without a corresponding acceleration in the rate of formation of volatile hydrogen suggests that these two elements do not come from the same compound. This conclusion is borne out by the observed differences in the activation energies of the reactions producing the two materials as shown in Table I. Moreover the ratio of the sensitivities of the reactions forming volatile hydrogen and volatile carbon compounds to decalin concentration is not as would be expected if the two elements were from the same volatile compound. In addition, although both reactions were catalyzed by the addition of 2% silicone to the decalin, the rate of formation of volatile carbon compounds was increased to 3.5 times the rate in pure decalin, whereas

the rate of formation of volatile hydrogen was only doubled. This could not be the case if the two elements were produced by the same compound. The authors were forced to conclude, therefore, that the carbon and hydrogen are actually from separate compounds.

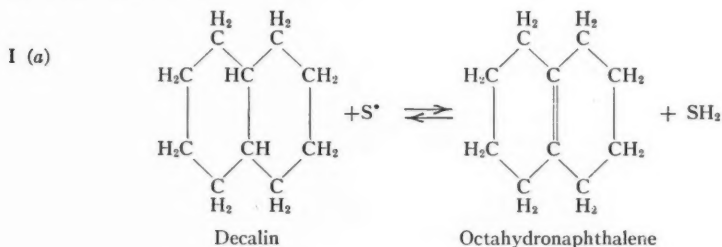
A review of the literature indicated that Kröger and Strüber (13) found carbon monoxide and hydrogen gas among the oxidation products of naphthenes. Chavanne *et al.* (2, 3, 4) reported the presence of carbon monoxide and hydrogen among the volatile oxidation products of methylcyclopentane and 1,4-dimethylcyclohexane when oxidized at 80° and 100° C. Fenske *et al.* (6) found carbon monoxide and hydrogen among the volatile oxidation products of lubricating oils and Larsen *et al.* (15) also found both gases among the oxidation products of hydrocarbons. Apparently, however, none of the authors have connected the presence of these gases with the initiating reaction.

It was assumed, therefore, that the volatile carbon compound measured is actually carbon monoxide gas and that the volatile hydrogen measured is actually hydrogen gas.

The appearance of 1-cyclohexene-1,2-dicarboxylic acid in the early stages of the reaction and its low, linear rate of formation with time suggested that it is also connected with the initiating reaction.

On this basis, the mechanism postulated for the initiating reaction involves the catalytic dehydrogenation of decalin to form octahydronaphthalene with its subsequent stepwise oxidation to 1-cyclohexene-1,2-dicarboxylic acid. The mechanism postulated produces water, carbon monoxide, and hydrogen gas in the observed ratios and accounts for the formation of decalin radicals which could initiate the oxygen-uptake reaction as shown later.

The first step postulated is the simple dehydrogenation of decalin catalyzed by the surface of the vessel:



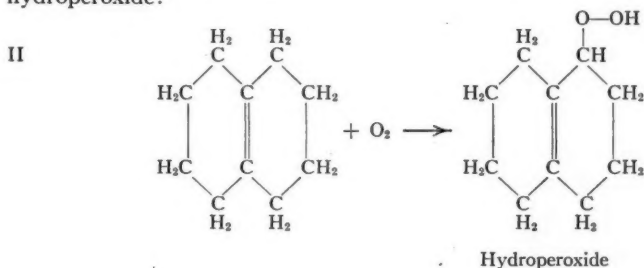
with the subsequent liberation of gaseous hydrogen:



This reaction occurs to a limited extent only. It is in accordance with the primary dehydrogenation theory postulated by Lewis (16). Waters (18) also postulates that the initial step in oxidation is the abstraction of neutral

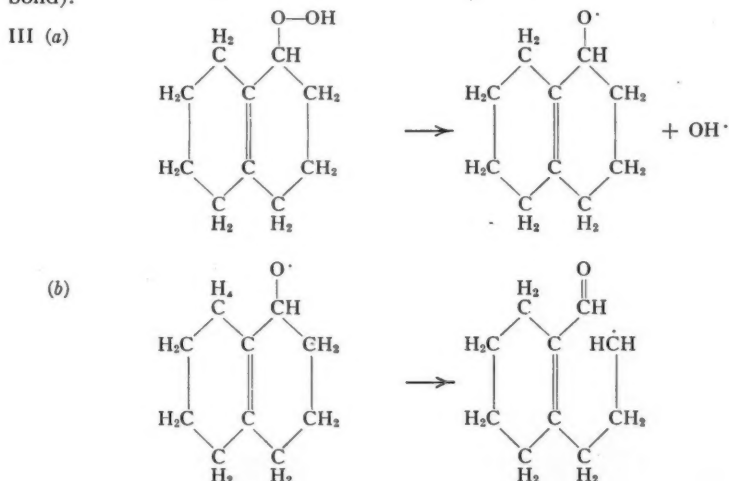
hydrogen. George and Robertson (7, 8) have shown that where no unsaturation exists, such as in decalin, the most labile hydrogen is that which is connected to a tertiary carbon atom. This would account for the abstraction of the two hydrogens from the tertiary carbon atoms.

The octahydronaphthalene formed is sensitive to oxidation, forming the hydroperoxide:

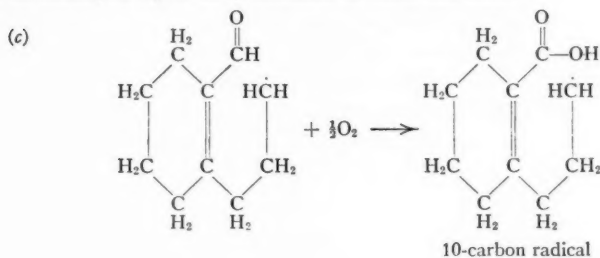


The suggested formation of the hydroperoxide on the α -position to the double bond is in accordance with the work of Farmer (5), who shows that the mechanism of addition of oxygen to an olefinic linkage is mainly by addition at the α -methyl carbon and not directly at the double bond, as frequently postulated. George and Robertson (7, 8) have also shown that the most likely point of attack by oxygen is at the weakest C—H link, which is on the carbon in the α -position to the double bond.

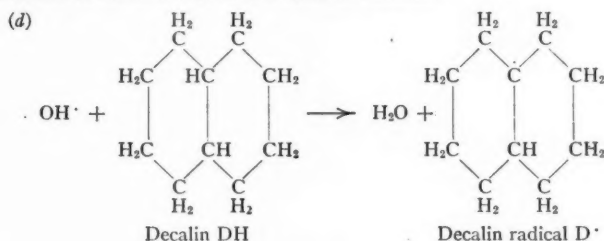
The hydroperoxide formed is unstable and decomposes by the mechanism postulated by George and Walsh (9), with splitting first at the O—O bond and then at the weakest adjacent bond of the α -carbon (other than the C—O bond).



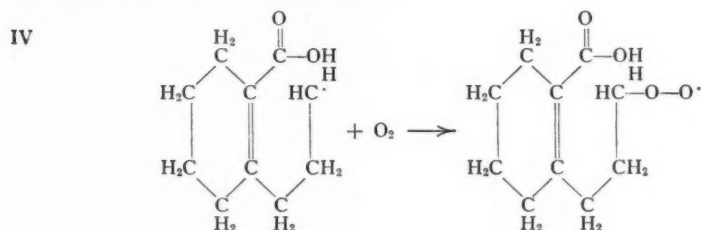
The aldehyde tip readily oxidizes to form the acid:



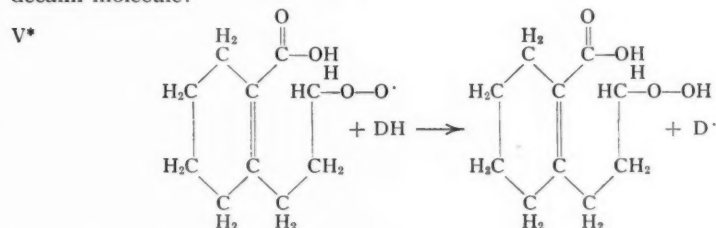
The hydroxyl group formed by Reaction III(a) can react with a molecule of decalin to form water and a decalin radical:



The active 10-carbon radical from III(c) combines with oxygen to form the hydroperoxide radical as follows:

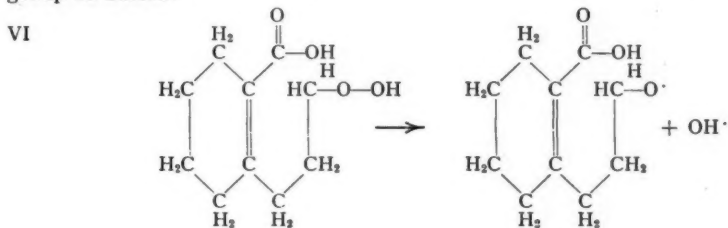


The hydroperoxide radical is capable of extracting hydrogen from another decalin molecule:

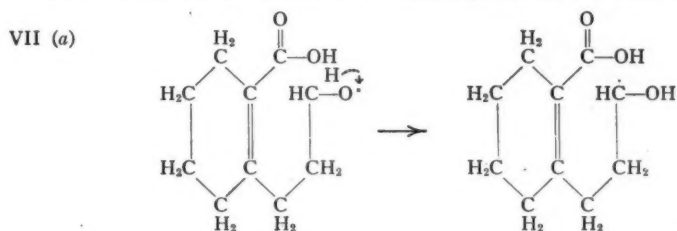


* The symbol "DH" is used here to represent a decalin molecule and "D·" to represent a decalin radical.

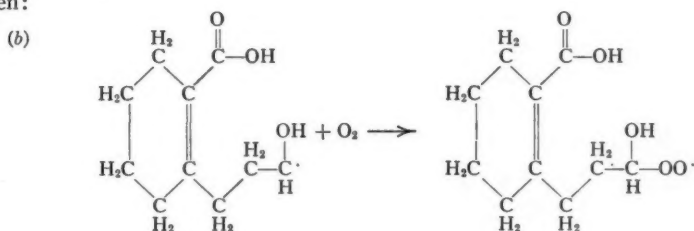
The hydroperoxide formed now decomposes with the loss of a hydroxyl group as before:



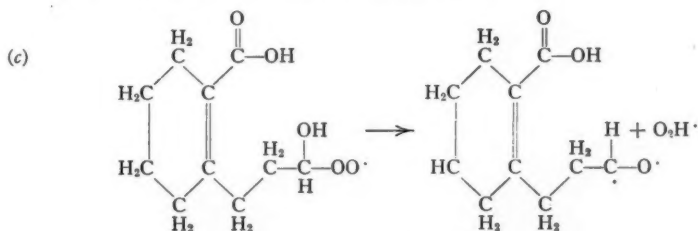
The aldehyde radical formed now rearranges with a 1,2 shift of hydrogen:



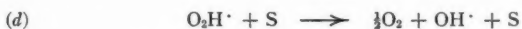
The rearranged radical is now capable of addition of another molecule of oxygen:



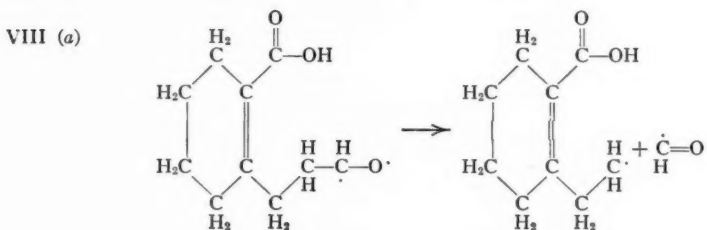
The highly oxygenated tip loses the radical $\text{O}_2\text{H}\cdot$:



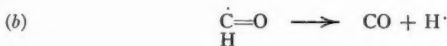
Step VII may be considered to be the abstraction of hydrogen from the radical by a molecule of oxygen. The radical O_2H^\cdot decomposes upon contact with the wall to form neutral oxygen and a hydroxyl group:



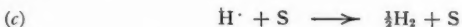
Another 1,2 hydrogen shift to the oxygen is now unlikely. Fission of the C—C bond follows, with the release of the formyl radical:



The formyl radical decomposes to form carbon monoxide and a hydrogen atom:

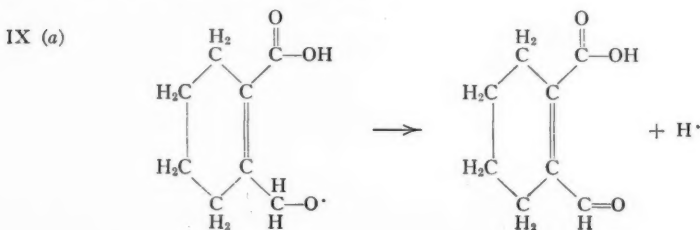


The hydrogen atom is recombined by contact with the surface of the vessel:

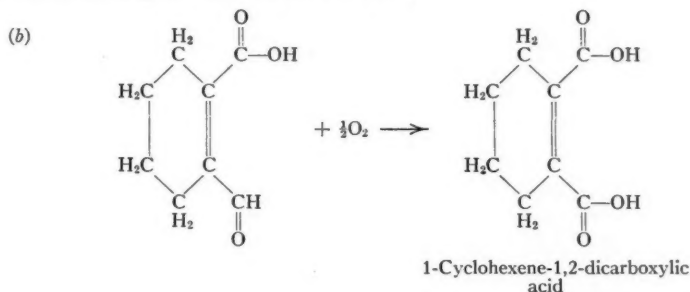


A 9-carbon radical now exists similar to the 10-carbon radical formed by Reaction III and it is capable of going through the same sequence of reactions IV to VIII to form a similar 8-carbon radical.

The results indicate that the destructive oxidation of the molecule stops at this point. It is possible that steps IV, V, and VI occur as before to form the 8-carbon aldehyde radical, but that owing to the influence of the ring or of the double bond, instead of the rearrangement of the aldehyde radical as shown in step VII, the radical stabilizes itself by the formation of the aldehyde group and the loss of a hydrogen atom:



followed by the oxidation of the aldehyde to form 1-cyclohexene-1,2-dicarboxylic acid found among the reaction products:



An independent check on the postulated mechanism for the initiating reaction is possible by comparing the amount of hydrogen formed with the amount that would be expected from the unsaturation in the 1-cyclohexene-1,2-dicarboxylic acid. At 100 hr. approximately 0.006 mole of the acid precipitated from the decalin (per liter) with unsaturation corresponding to 0.012 gm-atoms of hydrogen. At this time 0.064 gm-atoms of hydrogen was collected. However, from the proposed mechanism only two out of the five atoms of hydrogen formed by the complete oxidation of an octahydronaphthalene molecule to form the acid are from the unsaturation in the acid, so that only 0.025 gm-atoms of hydrogen would be expected from unsaturation in the acid.

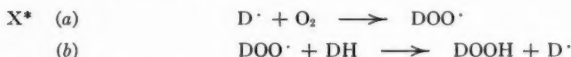
Since only a few milligrams of the acid was formed in each run (about 100 mgm. at 100 hr. in a 100 ml. sample of decalin) a small solubility of the acid in the decalin would make a large percentage error in the quantitative determination of the acid. Allowing for some solubility of the acid in the decalin and for the possibility that the oxidation of the octahydronaphthalene did not always go to completion, thus forming some hydrogen by the initial steps without the formation of a corresponding amount of the final acid, the values for the hydrogen obtained (0.025 gm-atoms at 100 hr.) and the hydrogen expected from an estimate of the unsaturation in the 1-cyclohexene-1,2-dicarboxylic acid (0.012 gm-atoms at 100 hr.) are considered to corroborate the postulated mechanism.

The initiating reaction that has been discussed represents only a small, although important, part of the over-all oxidation reaction. The 1-cyclohexene 1,2-dicarboxylic acid formed at 100 hr. of oxidation only accounts for 1.2% of the total oxygen consumed. However, the complete oxidation of one molecule of the octahydronaphthalene to form the acid results in the formation of nine decalin radicals, each of which is capable of initiating a reaction chain as shown below.

(b) Accelerated Period of Oxidation

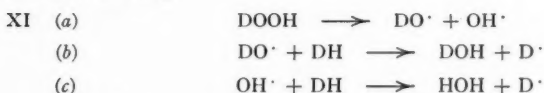
The initiating reaction postulated above provides a source of decalin radicals produced at an estimated rate of 11.4×10^{-4} mole D^\bullet per liter of

decalin per hour. It is generally believed (5, 11, 18) that oxygen uptake by hydrocarbons is by a radical-chain mechanism involving the hydroperoxide:



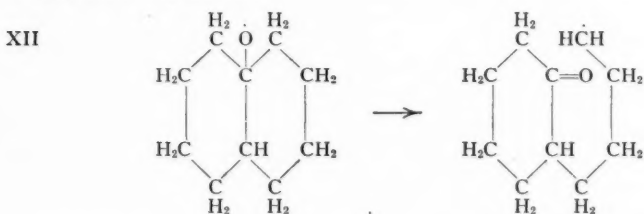
(Some authors (7, 8) however believe that an energy-chain mechanism will account for the facts.)

The hydroperoxide of decalin is known (10) to be a relatively stable compound, so that it would be expected to accumulate in the oxidized decalin. However, the results indicate that not over half of the total oxygen retained by the decalin is in the form of the hydroperoxide. It is postulated therefore that the hydroperoxide decomposes by a series of three reactions that lead to chain branching:



The chain branching resulting from the formation of two decalin radicals for each molecule of the hydroperoxide that decomposes accounts for the autocatalysis observed in the oxygen-retention reaction as shown in Fig. 5. Reaction XI (b) explains the presence of the saturated hydroxy compounds among the oxidation products. Reaction XI (c) explains the acceleration in the rate of water formation observed at 30 to 40 hours. It is assumed that the rate of hydroperoxide decomposition only becomes appreciable at that time. The similarity between the activation energy of the water-forming reaction in the initial and accelerated period is explained, since water is formed by the same reaction in each case.

The acceleration in the rate of formation of volatile carbon can be accounted for by rearrangement of some of the decalinol radicals produced by Reaction XI (a) with ring fission:



and further oxidation of the radical to form more complex compounds including carbon monoxide, acids, aldehydes, etc. Since there is no acceleration in the rate of formation of volatile carbon until 60 hr., Reaction XII cannot occur

*NOTE: The symbol DH is used here to represent a decalin molecule, D[·] to represent a decalin radical, DOO[·] to represent the decalin hydroperoxide radical and DOOH to represent decalin hydroperoxide. In later work the symbol DO[·] will be used to represent the decalinol radical and DOH will represent the decalinol molecule.

to an appreciable extent before this period. The difference between the activation energy observed for the reaction forming carbon monoxide in the initial and in the accelerated periods is explained by the difference in the reaction by which carbon monoxide is formed from the oxidation of octahydronaphthalene and the reaction by which it is formed from the oxidation of the decalinol radical.

Reaction XII explains the presence of carbonyl compounds formed in the accelerated period of the oxidation.

The chain-stopping reaction postulated is the combination of two decalin radicals with an oxygen molecule to form the peroxide:



The reactions X, XI, and XIII postulated to account for the reaction in the accelerated period cannot be a complete description of the accelerated oxidation mechanism, since when considered kinetically they do not explain the independence of the reaction to oxygen concentration nor its observed dependence on decalin concentration to the three-halves power. Moreover a kinetic analysis of these reactions suggests that the rate of oxygen uptake (including the oxygen going to form water) is twice the rate of water formation whereas the observed rate of oxygen uptake (including the oxygen going to form water) from Table I (412.5×10^{-4} mole oxygen per liter per hr.) is four times the rate of water formation (102.4×10^{-4} mole water per liter per hr.).

Part of the difficulty may be due to the assumption of homogeneity of the over-all reaction made in considering it kinetically. It seems quite possible that the oxygen uptake reactions X (a) and XIII are heterogeneous, occurring at the interface between the liquid decalin and the oxygen bubble. The rate of diffusion of the decalin radical to the interface of its orientation in the interface might be the rate-controlling step in the reaction chain X, making the reaction essentially independent of oxygen concentration. The apparent independence of the oxidation reaction to the amount of interface (pumping rate) between the oxygen and the decalin would be explained, qualitatively at least, by the chain-stopping reaction XIII, since chain-stopping as well as oxygen-uptake is dependent on the amount of interface.

Acknowledgments

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MÉTHODE DE SYNTHÈSE DE CÉTONES À PARTIR DES DÉRIVÉS ORGANOMAGNÉSIENS ET DES ORTHOESTERS¹

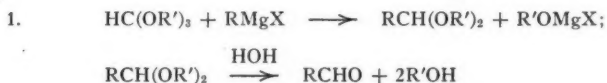
PAR ROGER BARRÉ ET BENOIT LADOUCEUR²

Sommaire

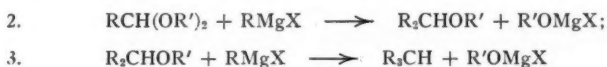
L'action des dérivés organomagnésiens sur les orthoesters fournit une méthode générale de préparation des cétones aliphatiques avec d'assez bons rendements dans plusieurs cas, les meilleurs étant obtenus avec les radicaux en chaîne droite. Avec l'orthocarbonate d'éthyle, on obtient seulement des cétones symétriques; avec les autres orthoesters, on obtient des cétones symétriques ou asymétriques suivant la nature de l'orthoester et du dérivé Grignard. Les rendements maxima (40 à 60%) sont obtenus avec un excès de deux molécules de dérivé organomagnésien par rapport à l'orthoester et un chauffage à reflux de huit heures en milieu étheré.

Introduction

Il se trouve dans la littérature chimique une méthode générale de synthèse des aldéhydes (2, 15, 17, 21) à partir des orthoformiates et des organomagnésiens:

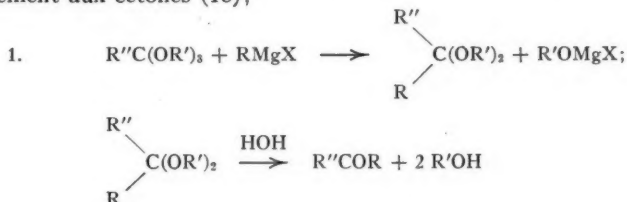


Théoriquement cette réaction peut se poursuivre (19) par réaction subséquente de l'acétal d'après les équations suivantes:



Elle peut conduire alors à des éthers-oxydes d'alcools secondaires et à des carbures.

Dans ces équations, il est possible de voir qu'en remplaçant les orthoformiates par leurs homologues supérieurs, les orthoesters, on peut arriver théoriquement aux cétones (18);

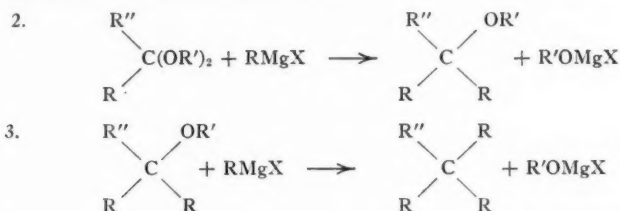


¹ Manuscrit reçu le 5 octobre 1948.

Contribution de l'Institut de Chimie de la Faculté des Sciences, Université de Montréal, Montréal, Qué.

² Adresse actuelle: Canadian Industries Limited, Beloeil, Que.

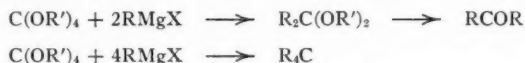
Théoriquement aussi, cette réaction peut se continuer et donner des éthers-oxydes d'alcools tertiaires et des carbures:



Les orthocarbonates peuvent aussi remplacer les orthoformiates et donner les mêmes réactions en passant, en une première phase (8, 18) par les orthoesters:



La réaction subséquente de ces orthoesters se confond avec celle donnée ci-haut. Mais il est à noter cependant que les orthocarbonates conduisent seulement à des cétones et à des carbures symétriques:



Nous avons voulu généraliser la réaction de préparation des aldéhydes par les dérivés Grignard et l'orthoformiate d'éthyle, en l'étendant aux cétones symétriques et asymétriques par l'action de ces mêmes dérivés sur l'orthocarbonate d'éthyle et les autres orthoesters.

Description des expériences

La préparation de cétones par l'action des organomagnésiens sur les orthocarbonates ou les orthoesters n'a pas encore été essayée lorsqu'on examine la littérature chimique. On a seulement préparé des orthoesters par l'action des organomagnésiens sur les orthocarbonates (8, 18). Pour arrêter la réaction à la première phase, on avait plutôt évité le contact prolongé des composés en présence ainsi que le chauffage de mélange après la condensation.

Comme nous voulions obtenir des cétons qui par hydrolyse donneraient des cétones soit avec les orthocarbonates soit avec les autres orthoesters, nous avons laissé la réaction se poursuivre librement puis nous avons cherché ensuite à la favoriser en faisant varier les conditions. Nous voulions cependant éviter les réactions conduisant aux éthers-oxydes et aux carbures.

L'étude de la réaction a été faite en utilisant d'abord l'orthocarbonate et l'orthopropionate d'éthyle, avec le bromure d'éthylmagnésium. Celui-ci a été fait à la façon habituelle dans l'éther éthylique anhydre et utilisé en solution étherée ou dans d'autres solvants substitués à l'éther; on opère en atmosphère d'azote. Les orthoesters ont été dilués dans leur volume du solvant employé et ajoutés lentement, en proportions variables, au bromure d'éthylmagnésium.

Après la condensation, le mélange a été traité par la chaleur, de différentes façons, puis le complexe organomagnésien formé dans la réaction a été décomposé à froid par l'eau, ensuite par l'acide sulfurique à 25%, qui en même temps hydrolyse le cétal en cétone; dans certains cas une solution aqueuse concentrée de chlorure d'ammonium (qui n'hydrolyse pas le cétal), nous a permis d'isoler ce dernier.

Les produits de la réaction (cétone ou cétal) ont alors été extraits à l'éther; les extraits ont été séchés sur Drierite et fractionnés par distillation. La cétone obtenue a été précipitée à l'état de semicarbazone par le chlorhydrate de semicarbazide. Le cétal, dans les cas où nous l'avons isolé, a dû être hydrolysé afin de libérer la cétone. Les semicarbazones séchées ont permis une identification des cétones synthétisées par leur point de fusion, et une évaluation des rendements obtenus, par leur pesée.

Partie expérimentale

Nous avons d'abord fait réagir les orthoesters et le bromure d'éthylmagnésium dans des proportions équimoléculaires puis nous avons utilisé par la suite un excès d'une à deux molécules de bromure d'éthylmagnésium.

a. Proportions équimoléculaires

Les premiers essais ont été faits dans l'éther anhydre, sans chauffer à reflux après la condensation terminée. Puis pour favoriser la réaction, nous avons chauffé à reflux plus ou moins longtemps (deux à huit heures). Nous avons ensuite élevé la température de réaction en substituant à l'éther après synthèse de l'organomagnésien, des solvants à point d'ébullition plus élevé (benzène, toluène). Enfin dans d'autres essais nous avons enlevé l'éther complètement par distillation (15) ce qui élève encore la température de réaction, soit immédiatement après la condensation ou soit après un chauffage à reflux de huit heures.

Malgré toutes ces variations de condition le rendement maximum en diéthylcétone a atteint 10% seulement de la théorie. Nous avons alors décidé d'utiliser un excès de l'organomagnésien par rapport à l'orthoester.

b. Excès d'une molécule d'organomagnésien

Des essais identiques à ceux décrits ci-haut ont été répétés. L'excès de l'organomagnésien s'est montré favorable à la réaction, car le rendement en diéthylcétone a passé de 10 à 35-40%. L'usage de solvants à haut point d'ébullition (benzène, etc.) au lieu de favoriser la réaction semble l'arrêter quelque peu car le rendement dans ces cas est resté inférieur à 30%. Le temps de chauffage à reflux après la condensation a varié de 4 à 16 h.; le temps optimum est de huit heures.

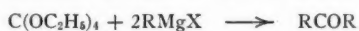
c. Excès de deux molécules d'organomagnésien

Quelques essais dans l'éther ont suffi à montrer que le rendement en diéthylcétone augmente encore un peu (5 à 10%) quand l'excès de bromure d'éthylmagnésium par rapport à l'orthoester est porté à deux molécules.

Dans ces conditions, i.e., condensation dans l'éther anhydre et chauffage à reflux subséquent de huit heures, plusieurs cétones ont été synthétisées.

Résultats

1. Avec l'orthocarbonate d'éthyle (cétones symétriques)



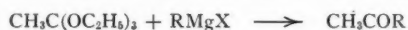
Cétones	Rendements, %	Semicarbazones	
		P.f. rapporté, °C.	P.f. obtenu, °C.
Diéthylcétone*	44	138-139 (10, 9)	137-139
Di- <i>n</i> -propylcétone	57	132-135 (16, 7)	132-132.5
Di- <i>i</i> -propylcétone	12 à 15	136 à 157 (13, 20)	134-136
Di- <i>n</i> -butylcétone	* 52	90 (11)	138-139 86-89

* Analyse—Calculé: C, 50.32; H, 9.14; N, 29.35%. Trouvé: C, 50.42, 50.62; H, 8.50-8.83; N, 29.31-29.37%.

Les di-*n*-amyl, di-*s*-butyl et di-*t*-butylcétones ont été synthétisées mais les rendements n'ont pu être évalués exactement car elles n'ont pas voulu donner de précipités avec la semicarbazide; les rendements des di-*s*-butyl et di-*t*-butyl cétones ont cependant été faibles car dans les deux cas l'organomagnésien n'a pas beaucoup réagi. Les dibenzyl et diphenylcétones n'ont été obtenues qu'avec un rendement inférieur à 20%.

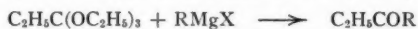
En essayant d'obtenir des composés non symétriques par réaction des orthocarbonates et de deux organomagnésiens différents, nous avons obtenu un mélange de cétones symétriques et non symétriques avec un mauvais rendement.

2. Avec l'orthoacétate d'éthyle (cétones avec un radical méthyl)



Cétones	Rendements, %	Semicarbazones	
		P.f. rapporté, °C.	P.f. obtenu, °C.
Méthyléthylcétone	6	135; 143 (11, 12)	142-143
Méthyl- <i>n</i> -propylcétone	17	100; 110 (14, 10)	100-102
Méthyl- <i>n</i> -butylcétone	29	118; 127 (10, 3)	123-125
Méthyl- <i>n</i> -amylcétone	31	122; 127 (4, 10)	121-122

3. Avec l'orthopropionate d'éthyle (cétones avec un radical éthyl)

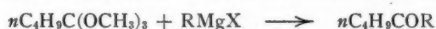


Cétones	Rendements, %	Semicarbazones	
		P.f. rapporté, °C.	P.f. obtenu, °C.
Diéthylcétone	45-52	138-139 (10, 9)	137-138
Ethyl- <i>n</i> -propylcétone	46	110-112 (1, 11)	108-110
Ethyl- <i>i</i> -propylcétone	20	80-95 (10, 6)	90-91
Ethyl- <i>n</i> -butylcétone	55	99-100 (11)	98-99
Ethyl- <i>i</i> -butylcétone	32	143 (5)	139-140 140-142
Ethyl- <i>n</i> -amylcétone	42	112-117 (11, 3)	110-111
Ethyl- <i>i</i> -amylcétone	40	132-133 (3)	119-120*
Ethyl- <i>n</i> -hexylcétone	43**	111-112 (11)	110-111
Ethyl- <i>n</i> -décylcétone	40	90- (11)	80-95

* Point de fusion bas même après plusieurs cristallisations; la substance obtenue est probablement un mélange d'isomères. Calculé: C, 58.39; H, 10.33; N, 22.68%. Trouvé: C, 58.53-58.57; H, 10.27-10.47; N, 21.94-22.01%.

** Rendement calculé d'après le poids de semicarbazone non purifiée.

L'éthyl-benzylcétone a été synthétisée avec 13% de rendement. L'éthyl-*s*-butylcétone a aussi été synthétisée mais avec un rendement inférieur.

4. Avec l'ortho-*n*-valérate de méthyle (cétones avec un radical butyl)

Cétones	Rendements, %	Semicarbazones	
		P.f. rapporté, °C.	P.f. obtenu, °C.
<i>n</i> -Butyléthylcétone	60	99-100 (11)	101-102
<i>n</i> -Butyl- <i>n</i> -amylcétone	39*	—	78-79

* Rendement calculé d'après le poids de semicarbazone non purifiée. Le point de fusion de cette semicarbazone n'est pas rapporté dans la littérature. Calculé: C, 61.93; H, 10.86; N, 19.70%. Trouvé: C, 61.79-61.86; H, 10.88-11.06; N, 19.66-19.69%.

Tous les dérivés halogénés utilisés dans les synthèses des organomagnésiens ont été des bromures sauf le dérivé benzyle qui a été employé sous forme de chlorure.

Dans la méthode de préparation des cétones décrites précédemment, l'addition d'un excès de dérivé organomagnésien par rapport à l'orthoester devrait en principe nous donner plus de réactions secondaires et par conséquent diminuer le rendement en produits cétoniques. Mais la bibliographie nous montre qu'il faut élever considérablement la température du reflux pour

effectuer le passage aux éthers oxydes secondaires et aux hydrocarbures prévus par la théorie. Nous l'avons d'ailleurs constaté dans la partie expérimentale; en effet, l'élévation de température de la réaction en changeant le solvant (benzène ou toluène à la place de l'éther) diminue les rendements. Au contraire, en faisant refluer à la température de l'ébullition de l'éther (36° C.), on peut limiter la réaction à la phase céta; cependant à cette température la réaction est lente et les produits formés très insolubles. C'est seulement par l'addition d'un excès de dérivé organomagnésien qu'on peut obtenir un rendement appréciable.

Remerciement

Nous tenons à remercier Canadian Industries Limited qui, par l'octroi à l'Université de Montréal d'une bourse de recherches dont Benoît Ladouceur fut le détenteur 1944 à 1947, a permis la poursuite de ce travail, partie des conditions requises pour l'obtention du grade de Ph. D.

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ORGANIC REAGENTS FOR PLATINUM METALS

I. THE DETERMINATION OF PALLADIUM WITH 1,10-PHENANTHROLINE¹

BY D. E. RYAN² AND P. FAINER

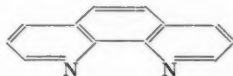
Abstract

Palladium may be precipitated quantitatively with 1,10-phenanthroline from palladous chloride solutions; variations in the hydrochloric acid concentration from 1 to 20% had no effect on the precipitation. The reagent yields no precipitates with other platinum metals under similar conditions; slightly high results, however, were obtained when palladium was precipitated from solutions containing these metals. The precipitate has the composition $C_{12}H_8N_2PdCl_2$ and may be used as a weighing form for palladium. A micro-volumetric method for palladium using 1,10-phenanthroline is described. Small amounts of platinum (as Pt^{+4}) do not interfere.

Introduction

The reactions of the platinum metals with various organic compounds have been studied extensively. Some of these reactions have formed the basis for analytical procedures for the platinum metals; many of the researches, however, have been concerned with the study of the methods of preparation and stereoisomerism of the various compounds produced. The present investigation was carried out with a view to extending the use of organic reagents for platinum metal determinations—and to relating the configuration of the organic compounds with their ability to react with these metals.

In a large series of preliminary experiments, 5-ml. aliquots of the standard platinum metal solution under investigation were diluted and acidified to six different acid conditions (0.05 and 0.30 *N* in hydrochloric acid, nitric acid, and aqua regia). The organic reagent was added and the solution gently boiled for two hours. If a precipitate formed, the mixture was filtered and the filtrate tested for the metal. As a result of this investigation, it was found that 1,10-phenanthroline



would precipitate palladium quantitatively from a hydrochloric acid solution of palladous chloride. No precipitates were obtained with solutions of Ru^{+3} , $Ir^{+4,+3}$, Rh^{+3} , Pt^{+4} under similar conditions.

¹ Manuscript received in original form August 25, 1948, and, as revised, November 9, 1948.

Contribution from the Department of Chemistry, University of New Brunswick, Fredericton, N.B., with financial assistance from the National Research Council of Canada.

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Gravimetric Determination of Palladium

Materials

1. Palladous chloride—solutions of palladous chloride standardized by dimethylglyoxime method (3).
Solution 1—6.96 mgm. palladium per 10 ml.
Solution 2—8.45 mgm. “ “ “ “
2. 1,10-Phenanthroline—0.5% aqueous solution.

Methods

To 10-ml. aliquots of the standard palladous chloride solution were added varying amounts of concentrated hydrochloric acid. Six milliliters of the 1,10-phenanthroline reagent was then added and the volume of the solution made up to 50 ml. These solutions were allowed to stand for one hour, and the precipitates were filtered through Whatman No. 42 filter papers, ignited in air, reduced in hydrogen, cooled in carbon dioxide, and weighed as the metal. The results are shown in Table I.

TABLE I

PRECIPITATION OF PALLADIUM WITH 1,10-PHENANTHROLINE AND SUBSEQUENT WEIGHING AS THE METAL

Palladium taken, mgm.	Palladium recovered, mgm.	Palladium taken, mgm.	Palladium recovered, mgm.
6.96	6.95	6.96	6.96
6.96	6.98	6.96	6.97
6.96	6.96	6.96	6.95
6.96	6.95	6.96	6.95
6.96	6.95	6.96*	6.88*
6.96	6.97	6.96**	6.90**
6.96	6.97		

* Average of several results in which no hydrochloric acid was added.

** Average of several results in which <4 ml. 1,10-phenanthroline was added.

In all other cases the hydrochloric acid concentration was varied from 1 to 20%.

Table I shows that palladium may be quantitatively precipitated with 1,10-phenanthroline from solutions varying from 1 to 20% in hydrochloric acid. Although 1,10-phenanthroline does not precipitate nickel or the platinum metals previously mentioned, under these conditions, it was found that results were 0.2 to 0.4 mgm. high in the presence of equivalent amounts of these metals.

In the absence of chloride ion, precipitates similar to the above were obtained in the presence of fluoride, bromide, or iodide. Palladous nitrate in dilute nitric acid also gave a precipitate with the reagent. This precipitate proved fairly soluble in water.

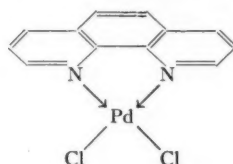
Composition of the Complex

Oven-dried (110° C.) samples of the complex were analyzed for palladium, for nitrogen (4), and for chlorine (1, 2). The results obtained, as shown in Table II, suggest that the complex consists of 1,10-phenanthroline, palladium, and chlorine in the ratio 1:1:2 respectively; this indicated a molecular formula $C_{12}H_8N_2PdCl_2$. The theoretical percentages for such a compound are also shown in Table II. The precipitate obtained from palladous nitrate and 1,10-phenanthroline suggested, on analysis, a similar structure, $C_{12}H_8N_2Pd(NO_3)_2$.

TABLE II
COMPOSITION OF COMPLEX

Composition	Per cent found	Number of determinations	Theoretical per cent for $C_{12}H_8N_2PdCl_2$
Palladium	29.2	8	29.8
Nitrogen	7.86	6	7.83
Chlorine	20.0	3	19.8

The dichloride proved extremely insoluble, even in nonpolar solvents. Dissolution in concentrated sulphuric acid and subsequent test with silver nitrate yielded a positive result for chloride ion. Aqueous solutions of the dinitrate complex yielded positive brown ring and diphenylamine tests for nitrate ion on standing. One would expect few ions to be present if no hydrolysis occurs in solution. Conductance measurements should help clear up this point, and further work is to be done in this direction. On the basis of analysis it seems probable that the structural formula of the complex is as follows:



Results obtained by filtering the precipitate through a fine sintered glass crucible, drying at 110° C., and weighing as $C_{12}H_8N_2PdCl_2$ are shown in Table III. These results indicate that palladium may be determined in this manner.

TABLE III
PRECIPITATION OF PALLADIUM WITH 1,10-PHENANTHROLINE AND SUBSEQUENT WEIGHING AS $C_{12}H_8N_2PdCl_2$

Palladium taken, mgm.	Palladium recovered, mgm.	Palladium taken, mgm.	Palladium recovered, mgm.
16.90	16.79	16.90	16.78
16.90	16.78	16.90	16.77

The Microvolumetric Determination of Palladium

Material and Equipment

1. Ferrous sulphate—analar grade,
2. Palladous chloride—standard solution containing 0.845 mgm. palladium per ml. and approximately 0.5% with respect to hydrochloric acid,
3. 1,10-phenanthroline—standard solution containing 1.00 mgm. of the monohydrate per ml.,
4. Hydrochloric acid—approximately 1:1 solution,
5. Fisher electrophotometer, AC model.

Development of Method

Since ferrous iron combines with 1,10-phenanthroline to form a soluble red ferrous phenanthroline complex, it was thought that palladium might be determined volumetrically by adding excess phenanthroline and determining this excess by measuring the color produced on addition of ferrous iron. Owing to the necessary acidity of the precipitating medium, it was found that a canary yellow color, instead of the familiar red ferrous phenanthroline color, was developed on addition of ferrous iron to the filtrate. The hue of the solution changed slowly with time and finally assumed the familiar reddish brown color. Any difficulty involved here was overcome by using a definite time interval before taking electrophotometer readings—both in the construction of a standard curve and in the actual analyses.

Preparation of Reference (or Standard) Curve

In constructing a reference curve, the following procedure was carried out. To x ml. of standard 1,10-phenanthroline were added a few drops of 1:1 hydrochloric acid and enough distilled water to make the final volume 100 ml. Approximately 0.1 gm. of analar grade ferrous sulphate (an excess) was added and the electrophotometer scale reading, using 425B filter, taken 15 min. after mixing.

Procedure

Samples of the standard palladous chloride solution were measured by means of a microburette into 250-ml. wide-mouthed Erlenmeyer flasks and the volume made up to approximately 25 to 30 ml. The standard 1,10-phenanthroline solution was added from a microburette, dropwise, until an excess of 2 to 4 ml. was present. After allowing to stand for one hour, the precipitate was filtered through a sintered glass crucible and washed well with distilled water. The volume of the filtrate was made up to 100 ml. in a volumetric flask, an excess of ferrous sulphate then added, and the color produced with the excess phenanthroline measured 15 min. after mixing. From the observed scale reading, the number of milliliters of standard phenanthroline added in excess can be determined by reference to the standard curve. Results are shown in Table IV.

The table shows that palladium may be determined quantitatively, even in the presence of small amounts of platinum or rhodium, by this method. Ions which also form complexes with 1,10-phenanthroline (as Cd^{++} , Cu^{++} , Zn^{++} , Co^{++} , Ni^{++} , Cr^{++} , Ru^{++} , etc.) must, of course, be absent. Further work regarding interferences is to be carried out.

TABLE IV
THE MICROVOLUMETRIC DETERMINATION OF PALLADIUM WITH
1,10-PHENANTHROLINE

Palladium taken, mgm.	Platinum metal added,* mgm.	Palladium found, mgm.
8.45	—	8.42
8.45	—	8.51
8.45	—	8.40
6.70	—	6.67
4.43	—	4.49
4.23	—	4.23
3.86	—	3.89
1.99	—	2.03
1.69	—	1.70
1.69	—	1.67
0.84	—	0.86
0.55	—	0.53
4.23	0.75 Pt	4.23
4.23	1.50 Pt	4.25
4.23	2.25 Pt	4.24
4.23	1.00 Rh	4.20
4.23	1.00 Rh	4.19

* Platinum added as H_2PtCl_6
Rhodium added as RhCl_3 .

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ORGANIC REAGENTS FOR PLATINUM METALS

II. THE GRAVIMETRIC DETERMINATION OF RHODIUM¹BY R. L. HAINES AND D. E. RYAN²

Abstract

Rhodium may be precipitated quantitatively with 2-mercaptobenzoxazole or 2-mercaptobenzothiazole. An acetic acid precipitating medium is preferred; slight variations in the concentration of acid, when nitric acid was used, caused low results. Several similar type organic compounds showed no advantages over the above two. The complex appears to have three molecular weights of the reagent combined with one atomic weight of rhodium.

Introduction

The reactions of organic sulphide compounds with many metals have been studied extensively. Currah and coworkers (1) investigated several organic sulphides as reagents for the platinum metals and reported the first organic precipitant, thiobarbituric acid, for rhodium. Among the large number of organic compounds undergoing preliminary investigation, in the authors' laboratories, were five mercapto compounds. The efficiency of these compounds for the precipitation of the platinum metals is being examined.

In all preliminary investigations, tests were carried out under varying acid concentrations (0.05 and 0.3 *N* in hydrochloric acid, nitric acid, and aqua regia). If, after boiling gently for two hours, a precipitate formed, the mixture was filtered and the filtrate spot tested (after destruction of organic matter) for the metal. The stannous chloride spot test was used for rhodium (3). Complete precipitation for rhodium with 2-mercaptobenzothiazole was found in 0.05 *N* nitric acid solution while other reagents—as 2-mercaptobenzoxazole and 2-mercapto-4-phenylthiazole—gave slightly low results. The following is a report of the successful application of 2-mercaptobenzothiazole and 2-mercaptobenzoxazole to the determination of rhodium.

Reagents

1. Rhodium trichloride—solution standardized with hydrogen sulphide (2).
2. 2-Mercaptobenzoxazole—solution containing 1.5 gm. in 100 ml. glacial acetic acid,
3. 2-Mercaptobenzothiazole—solution containing 1.5 gm. in 100 ml. glacial acetic acid,
4. Ammonium chloride—approximately 1% aqueous solution.

¹ Manuscript received in original form August 25, 1948, and, as revised, November 9, 1948.

Contribution from the Department of Chemistry, University of New Brunswick, Fredericton, N.B., with financial assistance from the National Research Council of Canada.

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Determination of Rhodium with 2-Mercaptobenzoxazole*Method*

To an aliquot of the standard rhodium solution in a 150 ml. beaker, 5 ml. of the ammonium chloride solution was added and the volume made up to approximately 50 ml. The solution was then heated to the boiling temperature and 3 to 4 ml. of the reagent added. After digestion for one hour at this temperature, the mixture, upon cooling, was filtered through Whatman No. 42 filter paper. The precipitate was washed with dilute acetic acid, ignited in air, reduced in hydrogen, cooled in carbon dioxide, and weighed as rhodium metal. Results are shown in Table I. The effect of different periods of digestion is also shown in Table I.

TABLE I
DETERMINATION OF RHODIUM WITH 2-MERCAPTOBENZOXAZOLE

Rhodium taken, mgm.	Rhodium recovered, mgm.	Digestion period, min.
11.35	10.08	10
11.35	10.37	10
11.35	11.02	20
11.35	10.81	20
11.35	11.12	45
11.35	11.25	45
11.35	11.34	60
11.35	11.41	60
11.35	11.37	60
11.35	11.34	60
11.35	11.30	60
11.35	11.33	60
11.35	11.40	60
11.35	11.36	60

Table I shows that rhodium may be determined quantitatively by this method but that a digestion period of at least one hour is necessary.

Composition of Complex

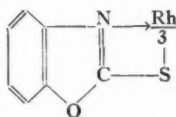
A rhodium precipitation was carried out with 2-mercaptobenzoxazole reagent. The precipitate was filtered, washed with dilute acid and water, dried under reduced pressure, and weighed. The residue was then ignited in air, reduced in hydrogen, cooled in carbon dioxide, and weighed as rhodium metal. Results are shown in Table II.

If three molecular weights of 2-mercaptobenzoxazole were combined with one atomic weight of rhodium, the latter replacing one hydrogen of each 2-mercaptobenzoxazole molecule, the amount of rhodium present would be 18.6%. Comparison of the complexes of metals with similar organic

TABLE II
COMPOSITION OF COMPLEX

Weight of complex, mgm.	Weight of rhodium, mgm.	Per cent rhodium
89.40	15.70	17.6
85.75	15.16	17.7
87.45	15.44	17.7
90.86	15.95	17.6
91.70	16.18	17.6

compounds leads to the conclusion that the above complex probably has the following structure:



Determination of Rhodium with 2-Mercaptobenzothiazole

Methods

The first experiments with this reagent were carried out using an alcoholic solution of the reagent and precipitating from a nitric acid (0.05 *N*) solution. Since slight variations in the concentration of this acid produced low results,

TABLE III

Determination No.	Rhodium taken, mgm.	Rhodium recovered, mgm.
1	7.34	7.40
2	7.34	7.33
3	7.34	7.37
4	7.34	7.36
5	7.34	7.32
6	7.34	7.38
7	7.34	7.37
8	7.77	7.77
9	7.77	7.80
10	7.77	7.70
11	7.77	7.80
12	7.77	7.73
13	13.97	13.96
14	13.97	13.97
15	13.97	13.93
16	13.97	13.91
17	13.97	14.03
18	13.97	13.91
19	11.35	11.35
20	11.35	11.33
21	11.35	11.39

Nos. 1-12: Alcoholic reagent solution and rhodium precipitated from 0.05 *N* nitric acid solution.

Nos. 13-18: Alcoholic reagent solution and rhodium precipitated from solution approximately 1 *N* in acetic acid.

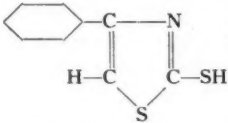
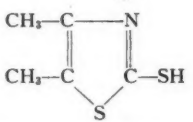
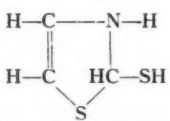
Nos. 19-21: Reagent dissolved in glacial acetic acid.

the method finally adopted was as with the benzoxazole. Results are shown in Table III.

It should be noted that the amount of reagent dissolved in acetic acid can be easily regulated. More or less reagent than the 1.5 gm. in 100 ml. of acid could be used, the actual quantity depending on the amount of rhodium to be precipitated. Slight variations in the acetic acid concentration had little effect on the degree of precipitation. The addition of ammonium chloride aided in the coagulation of the precipitate and made the precipitate more easily handled.

Three other compounds—with similar reactive groupings—were investigated to some extent. All these investigations were carried out in acetic acid media with the filtrates spot tested for rhodium. Results are shown in Table IV.

TABLE IV
SPOT TESTS WITH SIMILAR REAGENTS

Reagent	Formula	Acid strength			
		0.1 N	0.5 N	1.0 N	3.0 N
2-Mercapto-4-phenylthiazole		P	P	C	P
2-Mercapto-4,5-dimethylthiazole		P	P	P	N
2-Mercaptothiazoline		S	S	S	P

N No precipitation
S Very slight precipitation
P Partial precipitation
C Complete precipitation

These compounds show no advantages over the above reagents as precipitants for rhodium. In 3.0 *N* acetic acid medium, a strong red color was developed with 2-mercapto-4,5-dimethylthiazole; this might show promise as a colorimetric reagent for rhodium.

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THE DETERMINATION OF NITRATES IN COLORED SOIL EXTRACTS¹

F. J. SOWDEN AND H. J. ATKINSON

Abstract

In highly colored soil extracts, it was found impossible to determine nitrates directly by the phenoldisulphonic acid color reaction. Attempts to remove the coloring matter by oxidation or absorption were not successful. The most satisfactory method was found to be reduction of the nitrate to ammonia with Devarda's alloy in 0.1 *N* sodium hydroxide solution in the cold after the removal by steam distillation, of any ammonia that might be present in the extract. The ammonia formed from the nitrate was steam distilled into 0.01 *N* hydrochloric acid solution and determined colorimetrically by Nessler's reagent using a Klett-Summerson photoelectric colorimeter. The recovery of nitrates from the colored solutions and from standards was satisfactory. The aliquot taken for the determination should contain not more than 0.125 mgm. nitrogen as nitrate.

Introduction

The determination of the nitrate content of soils is usually made on an aliquot of a water extract by means of the phenoldisulphonic acid method (2). In order to obtain a clear solution, a small amount of the salt of a heavy metal, e.g., copper sulphate or aluminum sulphate (3), is added to the extractant as a flocculating agent and the extract is subsequently treated with calcium hydroxide to precipitate the hydroxides of the metals. This procedure is effective with the majority of soils.

Recently, during a nitrification study in which an ammonia-treated waste sulphite liquor product had been added to a soil (9), it was found impossible to obtain a clear extract in the above manner. The ligninsulphonic acids were water soluble and were not removed in the clarification process. For the nitrate color reactions, organic matter must be completely removed, as traces of organic materials give a considerable amount of color when the dried or concentrated extract is treated with phenoldisulphonic acid.

An attempt was made to remove the coloring material by absorption but neither the basic nor acidic amberlite resins, nor superfiltrol, would remove all the color. Charcoal from various sources would decolorize the solution but it also removed a large percentage of nitrogen from a standard solution of potassium nitrate, and the absorbed anion could not be freed from the charcoal by washing.

Oxidizing agents such as bromine and permanganate have been used to remove organic matter from soil extracts, but, in the present work, neither would sufficiently remove the ligninsulphonic acids to give a clear solution when the evaporated material was treated with phenoldisulphonic acid. Plice (6) suggested the use of superoxol and it was found that this would remove the

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organic matter, but the method was time-consuming, as repeated treatments were necessary. Moreover the results were very high owing to the presence of some nitrate nitrogen in the superoxol and to the oxidation of the ammonia in the waste sulphite liquor material to the nitrate form. The method might possibly be satisfactory where the soil extract contains large amounts of nitrates, very little ammonia, and organic material that is easily oxidized, but it was not satisfactory in this case.

Berge (1) has suggested that it is not necessary to remove the interfering color if a photoelectric colorimeter is available, as two aliquots can be evaporated to dryness and treated with the phenoldisulphonic acid. The color is developed in one of these and the other is used as a "blank" reading. Experiment showed, however, that the blank reading was very variable for identical aliquots. Thus, with low amounts of nitrate, the error might be very large and it was concluded that the method could not be used.

Experimental

In view of the failure of the above methods to remove the interfering color, it seemed that the alternative was to reduce the nitrate to ammonia, distill the ammonia from the colored solution, and determine it with Nessler's reagent. Olsen (4, 10) used Devarda's alloy (copper, aluminum, and zinc fused in a 50 : 45 : 5 ratio) to determine nitrate in soil, but his method required large quantities of nitrate. Pynne (7) has described methods for determining nitrate in plant materials using Devarda's alloy or titanous hydroxide for its reduction. With plant materials, any ammonia in the original material was distilled from calcium hydroxide and special precautions were taken to eliminate the possibility of any nitrogenous material being broken down to liberate ammonia. In the soil extracts in question, this interference was less likely to be serious but needed to be guarded against since some of the ammonia from the lignosulphonate was liberated by alkali and more by alkaline permanganate. Therefore, one of the methods suggested by Pynne was followed in principle although it was found necessary to make considerable changes in the details of the procedure to render it suitable for determining the small amounts of nitrate present in the soil extracts. The details of the method as finally adopted are as follows.

An aliquot (usually 20 ml.) was transferred to a 100 ml. Kjeldahl flask, made 0.1 *N* with sodium hydroxide, and steam distilled until there was no test for ammonia with Nessler's reagent, or until the distillate failed to change the color of two or three drops of methyl red in 10 or 15 ml. of water made acid with one drop of 0.01 *N* hydrochloric acid. Either test will detect traces of ammonia. The distillation was carried out in the apparatus described by Redemann (8). The ammonia was completely removed in three to five minutes, after which the flask was cooled. A small amount (approximately 0.5 ml.) of normal sodium hydroxide solution was added to compensate for the water that condensed during steam distillation, and 0.200 gm. of 100 mesh Devarda's alloy were introduced. The flask was stoppered with a rubber

stopper through which passed a glass tube containing glass wool wetted with 0.1 *N* hydrochloric acid to absorb any ammonia that might be carried away by the hydrogen evolved in the reaction. It was shaken several times at intervals of approximately 10 min., then left overnight. In the morning the acid was washed into the flask and the ammonia distilled into 5 ml. of 0.01 *N* hydrochloric acid until a volume of 35 to 40 ml. was obtained. It was found advisable to cut off the flow of steam to guard against any loss of ammonia while the Kjeldahl flask was being connected. The distillate was transferred to a 50 ml. volumetric flask, treated with 1 ml. of Nessler's reagent (prepared as described by Peters and Van Slyke (5)) and made to the mark. The optical density of the solution was then read in a Klett-Summerson photoelectric colorimeter using a blue filter. The concentration of ammonia in solution was obtained from a curve prepared by using a standard 0.001 *N* solution of ammonium sulphate, aliquots up to 25 ml. being treated with Nessler's reagent. A significant reading was obtained when the reagents only were used and this had to be deducted.

To test the accuracy of the method, a series of aliquots of a standard nitrate solution containing 0.01 mgm. nitrogen per ml. were analyzed. The recovery

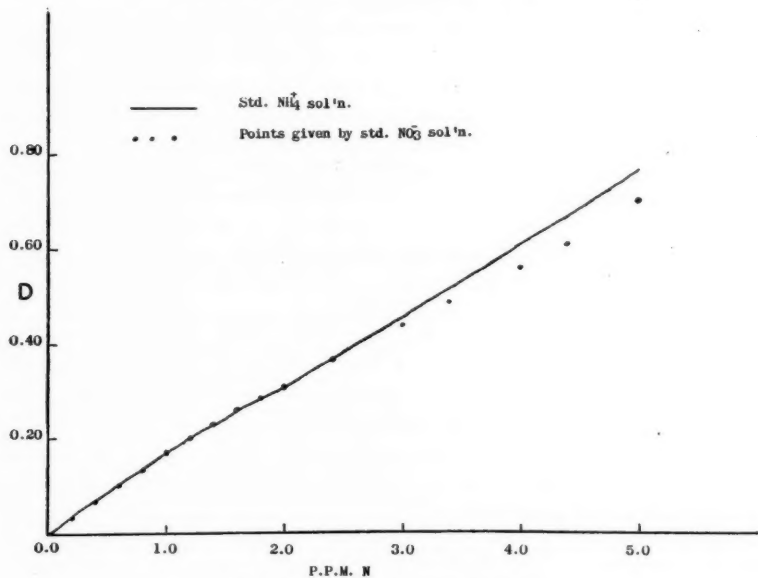


FIG. 1. Curve for standard solution.

is shown graphically in Fig. 1 where optical density is plotted against parts per million nitrogen. The solid line is the curve given by the standard ammonia solution calculated to parts per million nitrogen, and the circles show the density of color developed by the ammonia formed by reduction of

the nitrate. Most of the points on the curve represent averages of several determinations. The agreement was good up to 2.5 p.p.m. (0.125 mgm. nitrogen as nitrate). In this range the recovery was very close to the theoretical. The low recovery at higher concentrations appeared to be the result of incomplete distillation of the ammonia since, when the aliquot was doubled and 70 to 80 ml. was distilled and made up to 100 ml., the color formed was almost identical with that given when the procedure described in the method was followed. In general, it was found more satisfactory to use the smaller aliquot and keep the concentration below 2.5 p.p.m. nitrogen.

The nitrate curve in these higher concentrations seemed to be reproducible, however. In an experiment where known amounts of nitrate were added to soil extracts, good recovery was obtained as shown in Table I. As was to be

TABLE I
RECOVERY OF NITRATE ADDED TO SOIL EXTRACTS

Sample	p.p.m. N in soil extract	p.p.m. N added	Total p.p.m. N present	P.p.m. N recovered	
				NH ₄ curve	NO ₃ curve
A	2.60	2.00	4.60	4.15	4.57
B	2.40	2.00	4.40	4.05	4.47
C	1.65	2.00	3.65	3.45	3.70

expected, the recovery was low when the standard ammonia curve was used. If, however, the concentration was read from the nitrate curve to allow for the incomplete distillation of ammonia, the amount of nitrogen found was equal to the theoretical. Since this was an empirical correction, it seemed likely that good agreement was secured only because the distillation conditions were carefully standardized.

When small amounts of nitrate were added to two solutions of the waste sulphite liquor material from which the ammonia had been removed by distillation with alkali, results as shown in Table II were obtained. These would indicate that there was no breakdown of the organic material to yield ammonia on treatment with Devarda's alloy.

TABLE II
RECOVERY OF NITRATE ADDED TO SOLUTIONS OF WASTE SULPHITE LIQUOR SOLIDS

p.p.m. N added	P.p.m. N recovered	
	Solution A	Solution B
0.20	0.17	0.17
0.40	0.36	0.38
0.80	0.78	0.76

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THE PREPARATION OF CYANAMIDE, UREA, AND RELATED COMPOUNDS LABELED WITH LONG-LIVED RADIO-ACTIVE CARBON¹

BY S. H. ZBARSKY² AND ISABEL FISCHER

Abstract

The following compounds have been prepared labeled with C¹⁴: cyanamide, urea, thiourea, dicyandiamide, and guanidine nitrate. Cyanamide was synthesized by heating radioactive barium carbonate at 850° C. in a stream of ammonia and extracting with water the barium cyanamide so formed. Urea and thiourea were prepared from cyanamide by hydrolysis under suitable conditions. When an aqueous solution of cyanamide was heated, its dimer, dicyandiamide, was obtained and the latter compound was converted to guanidine nitrate by fusing with ammonium nitrate at 175° to 185° C. The preparations of the above materials were carried out on a 5 to 10 millimole scale, and good yields were obtained in each case.

Introduction

At the present time the long-lived radioactive isotope of carbon, C¹⁴, is supplied to investigators chiefly in the form of barium carbonate although other forms are becoming available.* Because of the limited value of barium carbonate or carbon dioxide in organic syntheses, it is often necessary to convert them to simple organic intermediates that can then be used in further syntheses. The present investigation into the synthesis of labeled cyanamide was undertaken because cyanamide appeared to be a most suitable intermediate in the synthesis of a number of compounds of biological interest, e.g., urea, guanidine, arginine, purines, and pyrimidines (1, 2, 3, 4, 5, 8). Furthermore, the methods described in the literature for the synthesis of cyanamide and its conversion to compounds related to urea were simple and could be applied in laboratories with limited facilities. Franklin (4) reported that when ammonia is passed over heated alkali carbonates, the latter are converted to the corresponding cyanamide salts from which cyanamide can be easily obtained (1, 2). In the present work this method has been developed for the synthesis of radioactive cyanamide from radioactive barium carbonate in 10 millimole quantities in yields of the order of 70%. Urea was prepared from labeled cyanamide by hydrolysis in an acid medium. By combining these two procedures so as to eliminate the necessity of first isolating cyanamide, a more direct and less time-consuming method was developed for the preparation of labeled urea. Thiourea was obtained by passing hydrogen sulphide through a heated acid solution of cyanamide in the presence of antimony pentasulphide (6). By heating a faintly ammoniacal solution of cyan-

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amide, dicyandiamide was prepared (1, 2), and the latter compound, when fused with ammonium nitrate, yielded guanidine nitrate (3).

In order to measure the radioactivity present in the synthesized compounds they were first oxidized and the carbon dioxide formed was precipitated as barium carbonate. The β -activity present in the barium carbonate samples was then measured using an end-window type of Geiger-Müller counter tube. It was found that the activities of the synthesized compounds agreed with that of the barium carbonate used as original starting material within the limits determined by the counting error. This finding indicated that in the preparations to be described there was no measurable loss of C^{14} due to exchange with carbon dioxide from the air and that the rates of reaction of the C^{12} and C^{14} compounds were not appreciably different.

Methods

In order to oxidize the carbon of the prepared compounds to carbon dioxide and to collect the gas, the method described by Van Slyke and Folch (7) was used. Weighed samples of the materials were oxidized by heating with a mixture of fuming sulphuric, phosphoric, chromic, and iodic acids, and the carbon dioxide produced was collected and measured quantitatively in a Van Slyke-Neill manometric apparatus. After the manometric readings had been taken to permit a quantitative determination of the carbon content of the sample oxidized, the carbon dioxide was expelled from the extraction chamber of the manometric apparatus and absorbed in 7 ml. of 4 *N* sodium hydroxide solution contained in a 15 ml. centrifuge tube. Preliminary experiments showed that by this procedure all except 0.2% of the C^{14} introduced into the extraction chamber as carbon dioxide could be forced out into the sodium hydroxide solution. Presumably the small residual activity was present in carbon dioxide adsorbed on the glass wall of the extraction chamber since it was possible to flush out the C^{14} with nonradioactive carbon dioxide.

The carbonate formed in the sodium hydroxide solution was precipitated by the dropwise addition of a saturated solution of barium chloride. The suspension of barium carbonate was centrifuged and the supernatant fluid was discarded. It was found that with the amounts of radioactive carbon used in the present work no measurable activity remained in the supernatant liquid. The precipitate was washed five times with small volumes of water. This washing was necessary in order to ensure the removal of excess alkali since it was found that the presence of alkali caused the formation of irregular layers of barium carbonate in the following stage of the procedure.

The barium carbonate in the centrifuge tube was suspended in a small volume of water (0.5 ml.) and the suspension was pipetted on to a weighed aluminum disk that had been cleaned and slightly etched by immersion in 5 *N* sodium hydroxide solution for one minute. The aluminum disk was $1\frac{1}{8}$ in. in diameter and 0.014 in. thick, with a flat, circular depression 1 in. in diameter and $\frac{1}{32}$ in. deep. The barium carbonate suspension was pipetted on to the disk so that it was confined to the circular depression. The disk was heated

under infra-red lamps the height of which was adjusted to permit slow drying of the precipitate. It was found that if drying occurs too rapidly, irregular layers form. When the suspension had dried to a sludge the disk was agitated slightly to spread the barium carbonate in a uniform layer. If the precipitate tended to accumulate along part of the circumference of the circular depression it could be made to move toward the center by tapping gently the opposite edge of the disk. The suspension was finally heated to complete dryness and a layer of barium carbonate was formed that was of uniform thickness and adhered strongly to the aluminum. The disk was then weighed again in order to obtain the weight of the layer of barium carbonate.

A study was also made of the use of organic solvents such as acetone and ethanol as agents in which to suspend the barium carbonate. It was found that acetone caused the barium carbonate to become granular and it then became difficult to prepare layers of uniform thickness. When ethanol was used extreme care was necessary to prevent the suspension from running over the edge of the disk. On the other hand, the surface tension of water is sufficiently great to keep the suspension within the circular depression of the disk. Furthermore, layers prepared from ethanol suspensions did not adhere to the aluminum as strongly as did those prepared from water suspensions.

The β -activity in the barium carbonate on the disk was measured using an end-window type, self-quenching Geiger-Müller counter connected to a "scale of 128"*. The counter had a mica window 1.25 in. in diameter and 2.1 mgm. per sq. cm. in thickness, and the aluminum disk was supported at a distance of 0.5 cm. from the window. A sufficient number of counts was recorded to ensure that the counting error was not greater than $\pm 1\%$. From the weight of the barium carbonate on the disk and the area over which it was spread, the thickness of the layer of barium carbonate was calculated in milligrams per square centimeter. The measured activity in the barium carbonate was then corrected to zero layer thickness by referring to a self-absorption curve (5). The activities of the various samples were calculated in terms of the number of counts per minute (extrapolated to zero layer thickness) per milligram of carbon present, and the activities of the prepared compounds were compared with that of the barium carbonate used as starting material on this basis. Each compound, except cyanamide, was crystallized to constant specific activity in order to remove any radioactivity due to traces of barium carbonate or carbon dioxide carried through the various procedures.

Nitrogen analyses were carried out using the micro-Kjeldahl procedure. All melting points were determined using a Fisher-Johns melting point apparatus.

Experimental

Cyanamide

Although it was pointed out by Franklin (4) that cyanamide could be prepared by passing dry ammonia over heated alkali carbonates, not many details were given of the method used. The following is an example of the

* Nuclear Instrument & Chemical Corporation, Chicago, Ill.

application of the procedure developed in the present investigation for the synthesis of radioactive cyanamide from radioactive barium carbonate.

Barium carbonate (3.11 gm.), giving 3165 counts per min. per mgm. of carbon, was weighed into a small platinum boat and the boat was placed in a quartz combustion tube in an electric furnace. Dry ammonia gas, prepared by warming concentrated ammonium hydroxide and passing the evolved gas first through a tube of soda lime and then through a tube containing sodium hydroxide pellets, was passed through the combustion tube. When the flow of ammonia had become rapid the combustion tube was heated to 850° C. and maintained at that temperature for three hours. The tube was then allowed to cool and the flow of ammonia was discontinued when the combustion tube reached room temperature. The platinum boat was removed from the tube and the fused contents was transferred to a small beaker and covered with 10 ml. of water. The mixture was cooled by immersion in an ice bath and stirred for 30 min. to break up any large lumps. An amount of ice-cold concentrated sulphuric acid equivalent to the barium present was then added dropwise and the mixture stirred for another hour. At intervals during this time the pH of the mixture was tested and, if the mixture had become alkaline, the pH was reduced to approximately 5.5 by the addition of hydrochloric acid. The mixture was centrifuged to remove as much of the solid material as possible and the supernatant liquid was transferred to a small round-bottomed flask. The precipitate in the centrifuge tube was washed several times with small volumes of water and the washings were added to the solution in the flask. This solution was then distilled to dryness under reduced pressure, care being taken not to allow the temperature of the contents to go above 40° C. The solid material that remained was extracted with several small portions of ether that were combined, the ether extract was evaporated to dryness, and the residue was then dried further *in vacuo* over phosphorus pentoxide. This residue was then extracted with dry ether and the crystalline material that remained after evaporation of the ether was dried *in vacuo* first over phosphorus pentoxide and then over sodium hydroxide pellets. The crystalline product weighed 487 mgm. (yield 73.5%) and melted at 40° C. Calc. for CH_2N_2 : C, 28.58; N, 66.62%. Found: C, 28.03, 28.05; N, 66.83%. Activity, 3075 counts per min. per mgm. C.

Because of the unstable nature of cyanamide it was not purified further but was used in other syntheses immediately after it was prepared.

Urea

Two methods were used to prepare urea labeled with C^{14} . In one method the compound was prepared from labeled cyanamide. In the second, urea was obtained from barium carbonate without first isolating the cyanamide, which occurs as an intermediate.

From Cyanamide.—Cyanamide (297 mgm.), having an activity of 3217 counts per min. per mgm. of carbon (prepared from barium carbonate with an activity of 3268 counts per min. per mgm. of carbon), was dissolved in

3 ml. of water and 0.5 ml. of concentrated hydrochloric acid. The solution was boiled under reflux for 10 min. then cooled and neutralized with sodium carbonate. The neutral solution was evaporated to dryness under reduced pressure and the residue was extracted with several small portions of boiling ethanol, which were combined. The ethanol extract was evaporated to dryness and the solid matter that remained was dried *in vacuo* over phosphorus pentoxide and then extracted with dry acetone in a micro-Soxhlet apparatus. The acetone was evaporated and the residue dried *in vacuo* over phosphorus pentoxide. The product weighed 388 mgm. (91% of theory; over-all yield from barium carbonate, 67%) and melted at 131° C. A mixture with an authentic sample of urea melted at 131° C. Calc. for CH_4N_2O : C, 20.00; N, 46.63%. Found: C, 20.19; N, 46.34%. Activity, 3244 counts per min. per mgm. C.

From Barium Carbonate.—Barium carbonate (3.10 gm.), having an activity of 3165 counts per min. per mgm. of carbon, was converted to cyanamide by the method already described. No attempt was made, however, to isolate the cyanamide. Instead, when the water extract had been distilled to dryness under reduced pressure, 3 ml. of water and 0.5 ml. of concentrated hydrochloric acid were added to the residue in the round-bottomed flask. The mixture was boiled under reflux for 10 min. and then cooled, neutralized, and evaporated to dryness. The residue was extracted as described in the preceding section to give 636 mgm. of urea (67.4% of theory) melting at 131° C. A mixture with authentic urea melted at 131.5° C. Calc. for CH_4N_2O : C, 20.00; N, 46.63%. Found: C, 20.20; N, 46.39%. Activity, 3101 counts per min. per mgm. C.

Thiourea

Thiourea was synthesized according to the method described by Plentl and Schoenheimer (6). Cyanamide (302 mgm.), with an activity of 3100 counts per min. per mgm. of carbon, was dissolved in 5 ml. of water and two drops of concentrated hydrochloric acid and 300 mgm. of antimony pentasulphide were added to the solution. A rapid stream of hydrogen sulphide was bubbled through the mixture while it was heated in a steam bath. This process was continued for two hours, after which time the mixture was boiled to remove excess hydrogen sulphide and filtered. The filtrate was neutralized with potassium carbonate and evaporated to dryness. The residue was crystallized twice from *n*-propanol to give 336 mgm. of thiourea (61.4% yield) melting at 174° C. A mixture with authentic thiourea melted at 174° C. Calc. for CH_4N_2S : C, 15.79; N, 36.82%. Found: C, 15.84; N, 36.38%. Activity, 3140 counts per min. per mgm. C.

Dicyandiamide

This compound was prepared by heating an aqueous solution of cyanamide in the presence of a small amount of ammonium hydroxide (1, 2, 8). Cyanamide (398 mgm.), with an activity of 2954 counts per min. per mgm. of carbon (prepared from barium carbonate with an activity of 2971 counts per min.

per mgm. of carbon), was dissolved in 4 ml. of water and 2 drops of concentrated ammonium hydroxide were added to the solution. The solution was boiled under reflux for four hours. It was then cooled and the crystals that separated out were collected on a sintered funnel and washed with several small portions of water that were added to the filtrate. A second crop of crystals was obtained by evaporating the filtrate to dryness and crystallizing the residue from water. A total yield of 350 mgm. of dicyandiamide (88% of theory) was obtained, m.p. 206° C. Calc. for $C_2H_4N_4$: C, 28.58; N, 66.62%. Found: C, 28.24, 28.28; N, 66.60%. Activity, 2966 counts per min. per mgm. C.

Guanidine Nitrate

The procedure employed for the preparation of guanidine nitrate was essentially that described by Davis (3). Dicyandiamide (405 mgm.), having an activity of 3246 counts per min. per mgm. of carbon, was weighed into a small, dry Pyrex test tube. Dry ammonium nitrate (900 mgm.) was added, the two materials were mixed thoroughly, and the mixture was then heated at 175° to 185° C. for three hours. During the period of heating, the mixture first melted to give a clear solution and then solidified. At the end of the heating period the contents of the test tube was cooled, dissolved in a small volume of warm water, and the solution was filtered to remove a small amount of insoluble material. The filtrate was evaporated to dryness and the residue crystallized from water. A further yield of crystals was obtained from the mother liquor. A total of 979 mgm. of guanidine nitrate (83% of theory) was obtained, m.p. 206° C. Calc. for $CH_6N_4O_3$: C, 9.84%. Found: 9.69%. Activity, 3286 counts per min. per mgm. C.

Acknowledgment

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THE ISOPIESTIC METHOD APPLIED TO SORPTION ISOTHERMS¹

BY S. BARNARTT² AND J. B. FERGUSON

Abstract

The isopiestic method has been applied to the sorption of carbon tetrachloride and water vapors by activated coconut shell charcoals. The isopiestic charges were found to be linearly related over wide pressure ranges. Isotherms formed by plotting the isopiestic charges of two charcoals one against the other consisted of three linear sections for both carbon tetrachloride and water. If the pressure isotherm of one charcoal be known, those of other charcoals may be computed from it by weighing relatively few isopiestic charges. Errors inherent in the measurement of equilibrium pressures, as well as those caused by the drift of the pressure isotherms towards higher sorption capacities at a given pressure, are eliminated in the isopiestic method of comparing charcoals. The linear relation between the isopiestic charges affords a simple criterion of rejection for equations proposed to fit the pressure isotherms. It also throws into relief the structural regularities in activated charcoals. The existence of discontinuities in the sorption process, reported by previous experimenters, is supported by the isopiestic data.

Introduction

The isopiestic method, introduced by Bousfield (3) and subsequently improved by Sinclair (14) and by Robinson and Sinclair (10), has been extensively used to obtain the thermodynamic properties of aqueous solutions. Its use has been almost wholly confined to such studies, however, although it is a general method applicable to all equilibria involving the taking up (sorbing) of a substance (sorbate) by another phase (sorbent) in contact with it. In a previous report (13) it has been shown that the sorption capacities of activated charcoals towards vapors may be tested simply and rapidly using the isopiestic method. Nearly-saturated vapors were studied therein. The present report compares the activities of charcoals towards vapors over wide vapor pressure ranges.

The isopiestic method compares two or more sorbents by placing them in the liquid or gaseous phase containing the sorbate, and allowing the latter to distribute itself among the sorbents until equilibrium is established. The relative activity of each sorbent towards the sorbate is then given by the concentration of the latter in the sorbent. The activities of two or more charcoals towards a given vapor at a given pressure may be determined directly by simply weighing the charcoals before and after sorption. Such activities will hereinafter be termed "isopiestic charges", expressed as Q milligrams of sorbate per gram of sorbent.

The activity of a sorbent towards a vapor at a given temperature is commonly recorded by plotting the equilibrium charge against the vapor pressure. If one such isotherm be known, that of another sorbent may be obtained by measuring a number of sets of isopiestic charges.

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Isopiestic charges of two sorbents may also be plotted one against the other. We have called this type of plot "isotherm of isopiestic charges", abbreviated to IIC. To avoid confusion, the common isotherm of charge against vapor pressure will be called "pressure isotherm".

Each point on the IIC gives a direct comparison of the activities of two sorbents under identical conditions. For sorption by charcoals, therefore, it might be expected that the IIC would throw into relief any similarities in the surface or pore structures of the two charcoals. This paper describes experiments designed to study the character of IIC's for charcoals and to reveal what type of information they might supply. Sorption of carbon tetrachloride and water vapors was investigated.

Experimental

Isopiestic Charges

Isopiestic charges were determined by the following procedure. The charcoal samples in tared weighing bottles were heated to 125° C. for approximately 24 hr. After cooling in a closed desiccator for 15 min. the bottles were capped and weighed to obtain the "dry weights" of the samples.

The dried charcoals were placed in a vacuum desiccator with a sample of the sorbate liquid and the desiccator evacuated until all the air was swept out by the evaporating liquid. The system was then isolated and the sorbate vapor allowed to distill into the charcoals.

Sufficient sorbate was used to saturate the charcoals in order to remove by displacement the volatile impurities held on them. In this connection Allmand and Chaplin (1, 4) have shown that the removal of gaseous impurities from the charcoal surface is more effectively done by presaturation with carbon tetrachloride than by subjecting the charcoals to high temperature evacuation.

The saturated charcoals were next desorbed by evacuation until a suitable quantity of sorbate was removed. The desiccator was placed in an insulated box whose temperature varied by $\pm 1^\circ$ C. After one to five days, depending on the relative pressure P/P_s (where P is the equilibrium pressure and P_s the vapor pressure of the sorbate at the temperature in question), the equilibrium charges on the charcoals were measured by weighing. The minimum time necessary for the attainment of equilibrium was determined in preliminary experiments by finding the time required for duplicate samples of the same charcoal, initially one "dry" and the other laden with sorbate, to attain the same charge within the degree of inhomogeneity of the charcoal samples. Subsequent sets of equilibrium charges were secured either by further desorption or by allowing more sorbate to distill into the charcoals.

Pressure Isotherms for Carbon Tetrachloride

In order to correlate the IIC's with pressure isotherms it was necessary to obtain the pressure isotherms for the sorption of each vapor by one of the charcoals. In the case of carbon tetrachloride this was done simultaneously with the measurement of isopiestic charges, using the apparatus shown in

Fig. 1. This apparatus yielded pressure isotherms for carbon tetrachloride over the relative pressure range $P/P_s = 10^{-3}$ to $P/P_s = 10^{-1}$.

The apparatus fitted into and was supported by the ground-glass joint atop the vacuum desiccator. The pressure in the system was measured by means

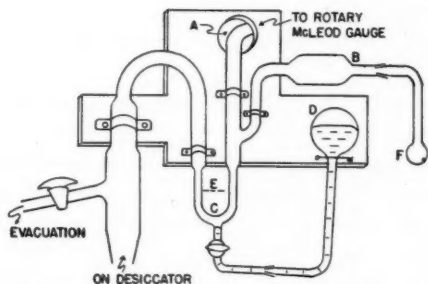


FIG. 1. Apparatus for measuring equilibrium pressures simultaneously with isopiestic charges.

of a rotary McLeod gauge reading from 0.0018 to 16 mm. of mercury. The gauge was positioned behind the wood support, the connecting tube being held tightly by the annular ring of rubber pressure tubing *A* inside the hole in the wood support. Tube *B* contained potassium hydroxide pellets for the removal of any carbon dioxide and water vapor from the vapor phase. The mercury cutoff *C* was operated by the small mercury reservoir *D* above which was a Torricellian vacuum. By swinging this reservoir down or up the cutoff was opened or closed.

When the pressure in the system became constant, a portion of the vapor phase was isolated by raising mercury to *E*. The carbon tetrachloride was frozen out by placing liquid air around bulb *F* and the residual pressure measured. In practice the residual pressures were small, ranging from 0.02 to 0.4 mm. of mercury. The total pressure of the vapor phase less the residual pressure gave the partial pressure of the carbon tetrachloride.

Pressure Isotherm for Water

The pressure isotherm for water was secured by isopiestic comparison of the charcoal with aqueous solutions. Sodium chloride solutions were used for the higher relative pressures, sulphuric acid solutions for the lower. Duplicate samples of the charcoal and of the solution were contained in four gold-plated silver dishes that were tapered to fit snugly into a silver-plated copper block inside the desiccator. This assembly and its application to isopiestic investigations has been described by Janis and Ferguson (8). The desiccator was evacuated carefully and allowed to rock gently in a water thermostat held at $25.0 (\pm 0.1)^{\circ}\text{C}$.

The relative pressures of the water vapor at equilibrium were obtained from the molality of the sodium chloride solutions using the activity data of Sheffer,

Janis, and Ferguson (12), and from the weight fraction of the sulphuric acid solutions using the activity data of Shankman and Gordon (11).

Materials Used

Charcoals: *A* was a steam activated coconut shell charcoal, impregnated with a catalyst.

B was an air activated coconut shell charcoal, impregnated with a catalyst.

C was an air activated coconut shell charcoal, impregnated with a catalyst.

D was an unimpregnated coconut shell charcoal.

Carbon tetrachloride. C.P. carbon tetrachloride, known to have methanol as chief impurity, was washed with water and distilled. $d_4^{25} = 1.592$.

Sodium chloride. "Kahlbaum Natriumchlorid 99.98%" was dried at 125° C. for two days. The dried product contained 0.2% water (Janis and Ferguson (8)).

Sulphuric acid. C.P. sulphuric acid was standardized by titration using anhydrous sodium carbonate (Analar "Analytical Reagent", purified by drying at 250° C. for 15 min.).

Results

Carbon Tetrachloride Isotherms

Isopiestic charges and simultaneous pressure measurements for charcoals *A* and *B* at 23° C. are presented in Table I, and the corresponding pressure isotherms in Fig. 2. Included also in the table are isopiestic charges outside the range of the measured pressure isotherms. All measurements are tabulated in chronological order.

The data within Groups I and III represent simple desorption points where the final operation on the system was evacuation of the charged charcoals, in the absence of free carbon tetrachloride liquid, until they were reduced to the charges shown. For Group II, however, the final operation was the distillation of carbon tetrachloride into the charcoals. In the latter procedure the carbon tetrachloride was frozen in bulb *F* (Fig. 1) using liquid air while the system was evacuated, then it was warmed and allowed to distill completely into the charcoals. Such determinations will be referred to as "adsorption" points.

Fig. 2 shows that these "adsorption" points all lay above the previous set of desorption points (Group I), indicating two distinct curves. The relative positions of the two curves, however, was the reverse of the usual adsorption-desorption hysteresis. Hence the charcoals have drifted towards higher activities at a given pressure, presumably a result of continuing evolution of gaseous impurities (1). The subsequent desorption points (Group III) confirmed the drift of the pressure isotherms, but indicated no further drift from

TABLE I

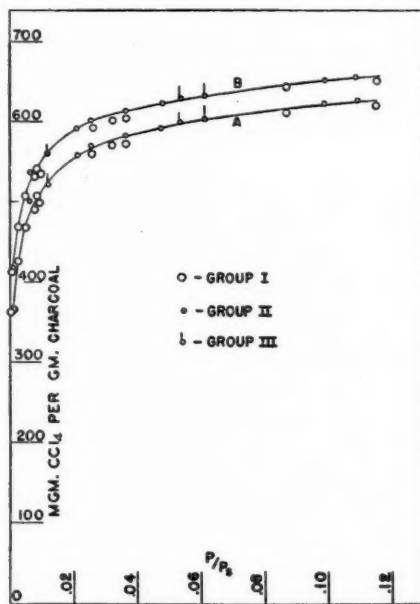
ISOPIESTIC SORPTION OF CARBON TETRACHLORIDE ON CHARCOALS *A* AND *B* AT 23° C.

Equilibrium pressure of CCl_4 , P , mm. of mercury	P/P_s^*	Mgm. carbon tetrachloride per gram charcoal			
		<i>A</i>		<i>B</i>	
		Sample 1	Sample 2	Sample 1	Sample 2
<i>Group I</i>					
0.92	0.0088	499	514	539	544
0.54	0.0051	461	473	505	508
0.27	0.0026	422	430	468	470
0.13	0.0012	363	368	413	415
12.1	0.115	608	634	644	655
0.98	0.0093	491	504	533	538
9.09	0.0867	600	624	637	652
2.64	0.0251	548	569	590	594
3.38	0.0322	560	580	598	604
3.84	0.0366	563	583	602	608
0.075	0.00071	360	365	412	413
0.83	0.0079	483	497	528	533
<i>Group II</i>					
11.4	0.109	616	640	654	661
0.69	0.0066	490	503	534	538
2.22	0.0212	548	569	591	595
2.67	0.0254	560	580	599	605
3.79	0.0361	573	594	612	617
5.00	0.0476	583	601	621	626
10.4	0.0991	609	637	648	657
<i>Group III</i>					
1.27	0.0121	514	530	557	562
5.60	0.0534	588	610	626	633
6.42	0.0612	593	616	630	637
<i>Group IV</i>					
	1	690	727	757	760
	1	698	736	766	769
		667	698	731	742
		644	672	695	702
<i>Group V</i>					
		Sample 3	Sample 4	Sample 3	Sample 4
		135	137	165	161
		189	189	223	221
		222	223	261	259
		248	248	292	289

* P_s = 105 mm. of mercury (7).

TABLE I—*Concluded*ISOPIESTIC SORPTION OF CARBON TETRACHLORIDE ON CHARCOALS *A* AND *B* AT 23° C.—*Concluded*

Equilibrium pressure of CCl_4 , P , mm. of mercury	P/P_s^*	Mgm. carbon tetrachloride per gram charcoal			
		A	B		
Group VI					
		Sample 5	Sample 6	Sample 5	Sample 6
		131	130	151	149
		298	292	342	343
		476	463	511	514
		Sample 7	Sample 8	Sample 7	Sample 8
		154	150	176	175
		196	190	226	226
		306	293	348	346
		511	487	540	538

* $P_s = 105$ mm. of mercury (7).FIG. 2. Pressure isotherms of carbon tetrachloride on charcoals *A* and *B*. 23° C.

Group II. The curves in Fig. 2 were therefore drawn to give preference to the points of Groups II and III.

The isopiestic charges of Table I are plotted as an isotherm of isopiestic charges in Fig. 3 (Curve I). The points of Group I are seen to lie on the same line as those of Groups II and III. Thus the IIC did not change as the pressure isotherms drifted towards higher activities at a given pressure.

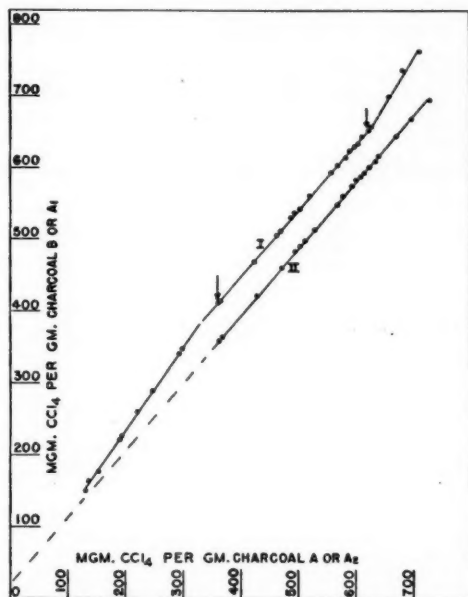


FIG. 3. Isotherms of isopiestic charges for the sorption of carbon tetrachloride by charcoals. 23° C. Curve I—Charcoals A and B. Curve II—"Duplicate" samples of charcoal A.

The low charges of Group V were obtained in the usual way except that the initial desorption of the presaturated charcoal samples was accelerated by heating the charcoals to 160° C. during the evacuation. Those of Group VI represent true adsorption points obtained by a continuous, slow distillation of carbon tetrachloride into charcoal samples that had not previously been exposed to it. The carbon tetrachloride was frozen in dry ice and allowed to distill *in vacuo* into the charcoal samples (at approximately 23° C.), the latter being weighed at intervals of one week. Since the distillation rate was minute, it was assumed that the charges on the charcoals at all times were the same as those for isopiestic equilibrium. This assumption is supported by the excellent agreement between Groups V and VI in Fig. 3. At very low pressures, therefore, true adsorption points yield the same IIC as desorption points.

As shown by Curve I, the IIC for the sorption of carbon tetrachloride by charcoals *A* and *B* can be represented accurately by three straight lines, over the pressure range from saturation down to an extremely minute value. The middle line includes the whole range of the measured pressure isotherms.

It should be noted that there was considerable inhomogeneity within each activated charcoal. The duplicate samples of charcoals *A* and *B* are seen from Table I to differ in activity by roughly 5% and 1% respectively as satu-

TABLE II
ISOPIESTIC CHARGES OF CARBON TETRACHLORIDE ON ACTIVATED CHARCOALS AT 23° C.
(Mgm. carbon tetrachloride per gram charcoal)

Charcoal C	Charcoal D	Charcoal B	Charcoal C
185	188	670	709
233	234	613	653
303	300	561	590
403	390	526	549
470	450	487	503
560	525	452	461
660	604	412	413
763	682		
774	Saturation 693		
774	Saturation 691		

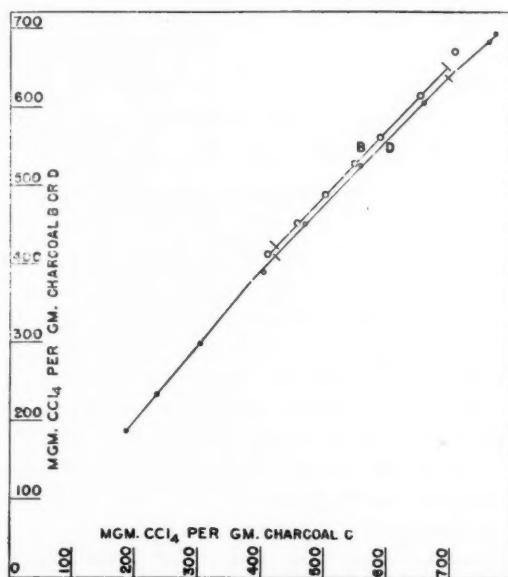


FIG. 4. Isotherms of isopiestic charges for the sorption of carbon tetrachloride, charcoals *B* and *D* vs. charcoal *C*. 23° C.

ration pressure is approached. This inhomogeneity was characteristic of all the charcoals studied, the duplicate samples exhibiting differences in activities ranging from 1% to 5%. The IIC for the duplicate samples of charcoal *A* is shown in Curve II, Fig. 3. Although these samples varied in activity by only 5% it was thought that the shape of the IIC would approximate that of two samples at different stages in the activation process. This IIC covers the pressure range from $P/P_s = 1$ down to $P/P_s = 0.0007$ and is a single straight line that extrapolates close to the origin.

Isopiestic charges of carbon tetrachloride on charcoals *B* and *C*, and *C* and *D*, are tabulated in Table II and plotted in Fig. 4. Over the range of the measured pressure isotherm for charcoal *B*, indicated by cross lines on each plot, both IIC's are linear. Theoretically, if the pressure isotherm of only charcoal *A* were known, those of *B*, *C*, and *D* could be computed after measuring as few as two sets of isopiestic charges within the pressure range in question.

Because of the linear relation between the isopiestic charges, the pressure isotherms of charcoals *C* and *D* will have the same general shape as those of charcoals *A* and *B* in Fig. 2.

Water Isotherms

The pressure isotherm for the sorption of water by charcoal *C* at 25.0° C. is presented in Table III and plotted in Fig. 5. Also shown in this figure is

TABLE III
PRESSURE ISOTHERM OF WATER ON CHARCOAL *C* AT 25.0° C.

Molality of NaCl solutions*	Weight fraction of H ₂ SO ₄ solutions*	P/P_s	Mgm. water per gram charcoal <i>C</i>		Time (days) allowed for equilibrium
			Sample 1	Sample 2	
3.18 6.145** 0.506		1	443	457	1
		0.885	411	426	16
		0.753	377	390	7
		0.983	428	441	16
		0.076	40	39	4
	0.667	0.259	56	55	4
	0.393	0.578	247	251	11
	0.528	0.291	77	76	3
	0.422	0.516	200	200	4

* Duplicate solutions agreed exactly to the third decimal place.

** Saturated solutions.

the pressure isotherm of charcoal *D*, obtained by isopiestic comparison with *C*. The isopiestic charges, Table IV, have been plotted as an IIC in Fig. 6.

Although the pressure isotherms for water differ so profoundly from those for carbon tetrachloride, the IIC's for these two sorbates are similar in that each may be represented by three straight lines.

TABLE IV

ISOPIESTIC CHARGES OF WATER ON ACTIVATED CHARCOALS AT 25° C.
(Mgm. water per gram charcoal)

Charcoal C	Charcoal D	Charcoal C	Charcoal D
15	17	315	308
61	39	207	179
105	58	149	105
140	92	91	64
360	344	426	394
380	363	224	214

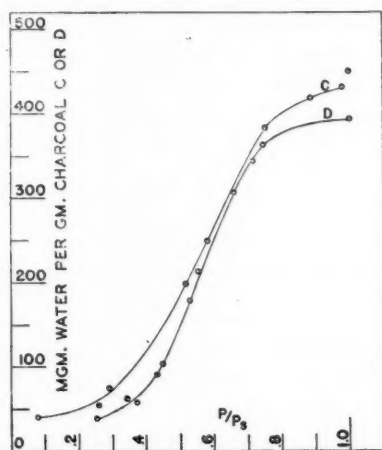


FIG. 5. Pressure isotherms of water on charcoals C and D. 25.0° C.

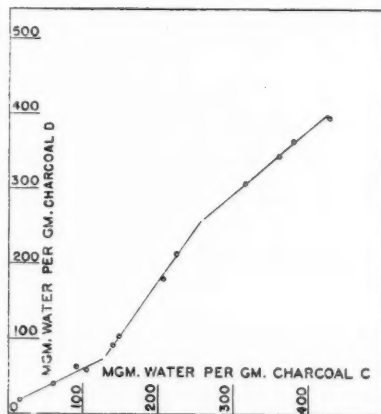


FIG. 6. Isotherm of isopiestic charges for the sorption of water by charcoals C and D. 25° C.

The isopiestic charges of the two samples of charcoal *C* in Table III are plotted as an IIC in Fig. 7. This IIC is seen to consist of two straight lines from zero charges to saturation. Thus, for water as for carbon tetrachloride, two samples of the same charcoal species have a simpler IIC than do two different charcoal species.

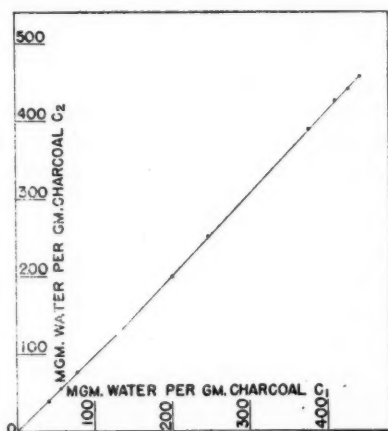


FIG. 7. Isotherm of isopiestic charges for the sorption of water by "duplicate" samples of charcoal *C*. 25.0° C.

Discussion

Discontinuous Sorption

The pressure isotherms obtained for the sorption of carbon tetrachloride by activated charcoals exhibit the same general shape as those that have been reported for carbon tetrachloride and many other vapors and gases (9, Chap. IV). A very careful investigation of the sorption of carbon tetrachloride at low pressures has been reported by Chaplin (4) and Allmand and Chaplin (1). At a carbon tetrachloride pressure of about 10^{-1} mm. and 25° C. (P/P_s of 0.00087), the pressure isotherms of their activated charcoals showed a discontinuous change with further increase in pressure. The heats of adsorption also showed a discontinuous change at about this pressure. The fact that the IIC's for our charcoals exhibit a discontinuity at a P/P_s just below 0.0007 substantiates the results of Allmand and Chaplin.

Further substantiation of this peculiarity is afforded by the data of Coolidge (5, 6). His typical isotherm for the sorption of an organic vapor by charcoal, plotted as Q vs. $\log P/P_s$, exhibits two points of inflection (6). The lower of these occurs at a P/P_s of roughly 10^{-3} , which is in agreement with the pressure isotherms of Allmand and Chaplin and with our IIC's. In addition, Coolidge's upper point of inflection occurs at a P/P_s of roughly 10^{-1} , which is in agreement with the upper discontinuity of our IIC's. It appears, therefore, that three equations would be required to describe the sorption of carbon tetrachloride by an activated charcoal over the whole pressure range.

Rejection Criterion

It has been shown that the IIC for the sorption of carbon tetrachloride by any pair of the four activated charcoals studied is a single straight line over the range of the measured pressure isotherm. This linear relation may be used as a criterion of rejection for equations proposed to fit the pressure isotherms. Let us propose, as an example, the Langmuir equation:

$$Q = \frac{aP}{1 + bP} \quad \text{or} \quad \frac{1}{P} = \frac{a}{Q} - b,$$

where a and b are constants. For isopiestic equilibrium between two charcoals Nos. 1 and 2, the Langmuir equation predicts that the reciprocals of the isopiestic charges are linearly related, since

$$\frac{1}{P} = \frac{a_1}{Q_1} - b_1 = \frac{a_2}{Q_2} - b_2.$$

This is not generally true if the isopiestic charges themselves are linearly related. In the special case where $b_1 = b_2$, however,

$$\frac{a_1}{Q_1} = \frac{a_2}{Q_2} \quad \text{or} \quad Q_1 = \frac{a_1}{a_2} \cdot Q_2,$$

and the IIC would be a straight line passing through the origin. Since our IIC's for carbon tetrachloride over the measured pressure range do not extrapolate through the origin, the Langmuir equation is mathematically inapplicable to our pressure isotherms. Similarly the Freundlich equation:

$$Q = c \cdot P^{1/n}$$

predicts that the logarithms of the isopiestic charges are linearly related and therefore is also inapplicable to our pressure isotherms. In confirmation, the four isotherms showed marked curvature when plotted either as $\frac{1}{P}$ vs. $\frac{1}{Q}$ or as $\log P$ vs. $\log Q$.

Theoretical Implications of Linear IIC's

Considering only the pressure range of the measured pressure isotherms for carbon tetrachloride, the following relations connect the isopiestic charges of the four charcoals studied:

$$Q_A = k_B + K_B \cdot Q_B = k_C + K_C \cdot Q_C = k_D + K_D \cdot Q_D,$$

where k 's and K 's are constants. It follows that

$$\frac{\Delta Q_A}{\Delta P} = K_B \cdot \frac{\Delta Q_B}{\Delta P} = K_C \cdot \frac{\Delta Q_C}{\Delta P} = K_D \cdot \frac{\Delta Q_D}{\Delta P}.$$

For a pressure increase from P to $P + \Delta P$, therefore, the corresponding increases in the charges on the four charcoals will be in the following proportions:

$$1 : \frac{1}{K_B} : \frac{1}{K_C} : \frac{1}{K_D}.$$

The above proportionality holds for any pressure increase ΔP , of any magnitude, within the range of the measured pressure isotherms. This would hardly be anticipated unless the same types of active surface were present in all four charcoals, each in the above-mentioned relative proportions.

The range of pressures over which this proportionality exists would be expected to be greater when comparing sorbents more closely related in composition and structure. Thus, two samples of a single charcoal species, prepared by the same activation process but activated to different extents, might exhibit a linear IIC over wider pressure ranges than do two of the different charcoal species studied here. In the limiting case where the activation process initially creates one or several types of active surfaces and then increases the concentrations of these uniformly without producing new types, one might anticipate IIC's that are single straight lines from zero pressure right up to saturation. Evidence, admittedly not very strong, that this limiting case may actually obtain in practice is afforded by Curve II, Fig. 3. This IIC, for two samples of the same charcoal species that differ in activity by about 5% at saturation, is one straight line from a P/P_s of 0.0007 up to saturation pressure and extrapolates close to the origin.

It is to be expected, therefore, that the IIC's for a series of charcoal samples representing the same starting material at different stages of an activation process would throw considerable light upon the activation mechanism. Such a series of charcoals has been investigated (2).

Conclusions

When the pressure isotherm for the sorption of a given vapor by one charcoal is known, the isopiestic method is an expedient means of obtaining the pressure isotherms of other charcoals. The existence of linear relations between the isopiestic charges, extending over wide pressure ranges, permits the computation of complete pressure isotherms by weighing relatively few isopiestic charges.

A comparison of the activities of two charcoals from individually measured pressure isotherms is subject to errors inherent in the measurement of equilibrium pressures and to errors caused by the drift towards higher charges at a given pressure. These inaccuracies are eliminated in the isopiestic method.

The linear relation between the isopiestic charges affords a simple criterion of rejection for equations proposed to fit the pressure isotherms. It also throws into relief the structural regularities in activated charcoals.

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AN ISOPIESTIC INVESTIGATION OF CHARCOAL ACTIVATION¹BY S. BARNARTT² AND J. B. FERGUSON

Abstract

The isopiestic method was used to study the sorption of carbon tetrachloride, water, methanol, and toluene by a series of charcoals representing the same coconut shell source at different stages of steam activation. The sorption of water by two charcoals of this series impregnated with benzoic acid was similarly investigated. The isopiestic charges of this activation series of charcoals were linearly related over wider pressure ranges than were those of unrelated charcoals. The activation process was found to be connected primarily with the principal pressure range over which single straight lines were obtained on plotting the isopiestic charges one against the other. The isopiestic data presented the following picture of charcoal activation. The activation process has created surfaces, probably of a heterogeneous character, which are active to all the four vapors studied. At any stage of activation these surfaces take up proportionate quantities, but not equal liquid volumes, of each sorbate at saturation pressure. The various types of surfaces increase in abundance with activation at the same relative rate, so that they are always present in the charcoal in the same relative proportions, up to a certain stage of activation. At this stage the production of the surfaces active at relatively low pressures begins to decline. This indicates that new pores are being created more slowly in comparison with the widening of existing pores. In addition to the active surfaces just described, the activation process produces some chemically selective centers which are active at minute relative pressures. The water sorption data discredit the theory of capillary condensation.

Introduction

The application of the isopiestic method to the sorption of vapors by activated charcoals has been described (5). For conditions of isopiestic equilibrium, the "charges" (milligrams of sorbate per gram of sorbent) on two charcoals were found to be linearly related over wide pressure ranges. This linear relation revealed structural regularities in the two charcoals.

For the sorption of either carbon tetrachloride or water by two charcoals, the isotherm formed by plotting the isopiestic charges one against the other (termed "isotherm of isopiestic charges", abbreviated to IIC) was found to consist of three linear sections. The IIC's were even simpler for two samples of the same charcoal which had somewhat different activities. It was thought, therefore, that the IIC's for the sorption of vapors by a series of charcoals, representing the same starting material at different stages in the activation process, would yield information about the activation mechanism. This report deals with an isopiestic study of such a charcoal series.

The sorption of carbon tetrachloride and water vapors by the end member of this series (charcoal *D*) has already been reported (5). The IIC's comparing charcoal *D* with other charcoals not closely related to it were found to comprise three straight lines. Those comparing charcoal *D* with members

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of the activation series should have simpler construction if the linear relation between isopiestic charges reflects structural regularities in the charcoals.

Isopiestic sorption of carbon tetrachloride, water, methanol, and toluene vapors by the charcoal series has been investigated. The sorption of water by two charcoals of the series which were first impregnated with benzoic acid has also been studied. The IIC's for water, especially on charcoals whose internal structure has been modified, should provide a test for the validity of the controversial capillary condensation theory.

Experimental

Isopiestic Charges

Using the method previously described (5), samples of the whole series of charcoals were charged with sorbate and equilibrated simultaneously.

Impregnation with Benzoic Acid

Five grams of the dried, granular charcoal were stirred into 1 liter of benzoic acid solution containing 1 gm. of benzoic acid. After 24 hr. of occasional stirring, the supernatant liquid was decanted. The charcoal was washed twice with 20 ml. of distilled water, then dried at 125° C.

By this treatment some of the charcoal fines were lost on decantation, and a small amount of water was retained by the treated charcoals even after drying at 125° C. The total change in weight resulting from these two factors was determined by running a "blank" for each charcoal whereby distilled water replaced the benzoic acid solution. The "blank" charcoal accompanied the impregnated one in the isopiestic experiments.

Materials

(1) Benzoic acid—Kahlbaum's.

(2) Charcoals—The coconut shell charcoals *C* and *D* have been previously described (5). The latter was the end member of an activation series of charcoals: *D*1, *D*2, *D*3, *D*4, *D*5, *D*6, and *D*. Charcoals *D*1–*D*6 were samples removed from the steam activator at successive intervals during the activation of *D*. Charcoal *D* was nearly completely activated, i.e., further steam treatment would reduce its activity. Certain properties of this charcoal series are given in a recent paper by Lemieux and Morrison (10), who investigated the sorption of aliphatic acids from aqueous solutions. It should be noted that these authors designated the series by the numbers: 1, 2, 3, 5, 6, 7, and 8 respectively. Another member of the series which they designated charcoal 4 has been omitted by us because it proved to be practically identical with *D*4.

(3) Methanol—Absolute methanol was purified by the method of Lund and Bjerrum (11) to a purity of 99.8% by density.

(4) Toluene—B.D.H. "Certified Chemical" grade.

Results

Sorption of Carbon Tetrachloride

The isopiestic charges of carbon tetrachloride on the activation series of charcoals are tabulated in Table I. They are plotted as IIC's in Fig. 1 in

TABLE I
ISOPIESTIC CHARGES OF CARBON TETRACHLORIDE ON THE *D*-CHARCOALS AT 23° C.
(Mgm. carbon tetrachloride per gram charcoal)

D1	D2	D3	D4	D5	D6	D
32	60	81	124	169	182	188
39	73	98	149	204	223	234
47	88	120	184	252	280	300
55	105	144	224	312	350	390
62	116	160	250	348	396	450
68	129	178	279	392	449	525
75	144	199	312	438	506	604
92	171	230	357	491	566	682
*96	183	244	371	508	577	692

* Saturation.

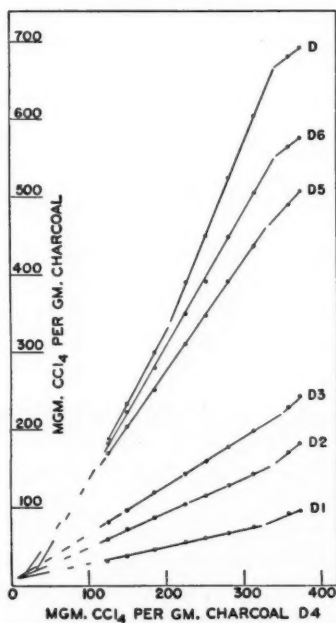


FIG. 1. Isotherms of isopiestic charges for the sorption of carbon tetrachloride by the activation series of charcoals. 23° C.

which each charcoal is compared to *D*4, the middle member of the series. Pressure isotherms for the charcoal series have been computed from Fig. 1 and the known (5) pressure isotherm for charcoal *D*. These are shown in Fig. 2.

The IIC's for the first six charcoals of the series are seen to be single straight lines from a low charge, representing a minute relative pressure, up to a charge representing a P/P_s of roughly 10^{-1} . These lines extrapolate approximately

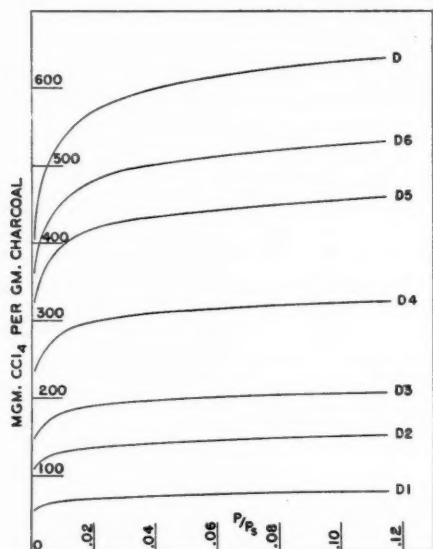


FIG. 2. Pressure isotherms of carbon tetrachloride on the activation series of charcoals. 23°C .

to a point close to the origin. The IIC for charcoal *D* compared with *D4*, and hence also if compared with any one of the first six charcoals of the series, contains a second discontinuity, thus resembling those previously reported for two "unrelated" charcoals (5).

Sorption of Water

The isopiestic charges of water on the series of charcoals are tabulated in Table II and plotted as IIC's in Fig. 3. Pressure isotherms for the charcoal series have been computed from Fig. 3 and the pressure isotherm for charcoal *D* (5). These are shown in Fig. 4.

The IIC's for the charcoal series are all composed of two linear portions, the lower one passing through the origin and the upper through saturation. Thus for water as for carbon tetrachloride, they are simpler than the IIC's of unrelated charcoals. The discontinuity in these IIC's occurs at charges that are approximately the points of inflection of the pressure isotherms. These charges represent roughly the same pressure, P^1 in Fig. 3, a relative pressure of 0.47. The lower line of each IIC is close to the 45° line; hence the activation process has produced little change in the activity of the charcoal over the P/P_s range 0 to 0.47.

The isopiestic data for the sorption of water by charcoals D4 and D6 impregnated with benzoic acid, and by the corresponding "blank" charcoals,

TABLE II
ISOPIESTIC CHARGES OF WATER ON THE D-CHARCOALS AT 25° C.
(Mgm. water per gram charcoal)

D1	D2	D3	D4	D5	D6	D
13	13	15	16	17	17	17
36	34	38	39	39	39	39
56	55	58	61	63	60	58
91	92	97	105	108	100	92
170	190	204	242	276	309	344
172	193	208	249	287	329	363
156	174	187	220	251	284	308
130	143	152	167	180	182	179
84	89	93	102	108	107	105
54	55	58	63	66	65	64
*183	206	221	266	307	354	394
132	145	156	176	197	210	214

* Saturation

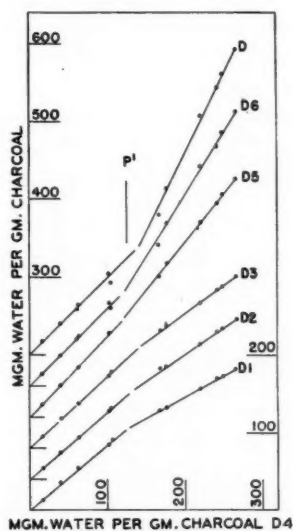


FIG. 3.

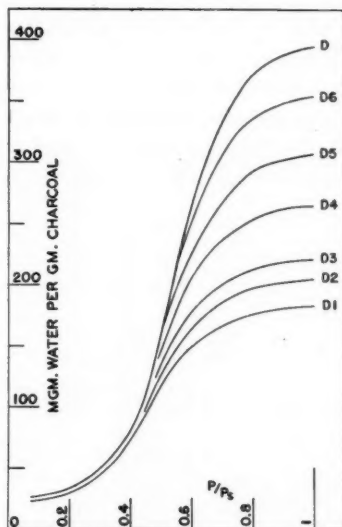


FIG. 4.

FIG. 3. Isotherms of isopiestic charges for the sorption of water by the activation series of charcoals. 25° C.

NOTE: For clarity the curves are separated by ordinate displacement. To obtain true ordinates:

Curve number

D1 D2 D3 D5 D6 D

Subtract from ordinate reading

0 40 80 120 160 200

FIG. 4. Pressure isotherms of water on the activation series of charcoals. 25° C.

TABLE III
ISOPIESTIC SORPTION OF WATER VAPOR BY CHARCOALS *D4* AND *D6*
IMPREGNATED WITH BENZOIC ACID. 25° C.

P/P_s	Isopiestic charges, mgm. water per gram charcoal			
	<i>D4</i> impregnated	<i>D4</i> blank	<i>D6</i> impregnated	<i>D6</i> blank
1	177	277	258	359
0.79	163	260	236	338
0.77	161	257	233	332
0.64	128	212	174	258
0.57	114	177	140	200
0.55	109	155	131	167
0.50	91	112	102	108
0.46	83	93	90	87
0.345	46	46	46	42
—	15	12	15	12

are tabulated in Table III. The impregnation treatment resulted in the sorption of 117 mgm. benzoic acid per gram of charcoal *D4*, and 135 mgm. benzoic acid per gram of *D6*. The isopiestic charges of water on the impregnated charcoals shown in Table III were calculated as: (mgm. water)/(grams of impregnated charcoal less grams of benzoic acid thereon); hence all the charges for water refer to 1 gm. of dry unimpregnated charcoal.

The equilibrium pressures of Table III were given by samples of charcoal *C* equilibrated simultaneously. Pressure isotherms for the impregnated charcoals are shown in Fig. 5. They are similar in shape to those of Fig. 4, except

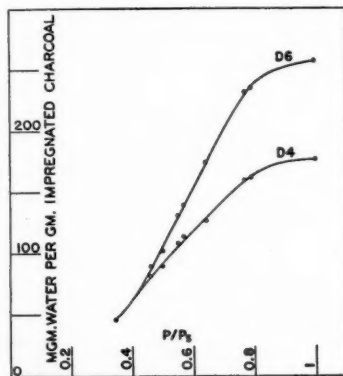


FIG. 5. Pressure isotherms of water on charcoals impregnated with benzoic acid. 25° C.

that the relatively rapid increase in sorption between $P/P_s = 0.45$ and $P/P_s = 0.65$ is somewhat more gradual. This is clearly evident from the IIC's in Fig. 6, the middle linear sections of which correspond to the relative

pressure range 0.45 to 0.65 and exhibit much greater sorption for the blank charcoals. Nevertheless the IIC comparing the two impregnated charcoals, shown in Fig. 7, is two straight lines from zero charge to saturation, the same as the IIC for the blanks.

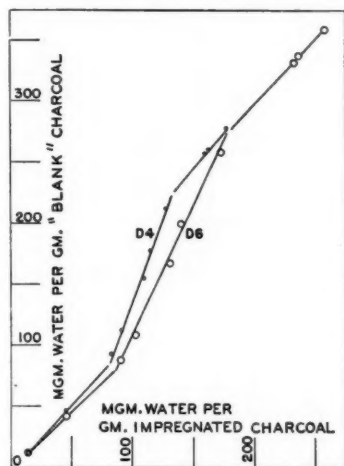


FIG. 6.

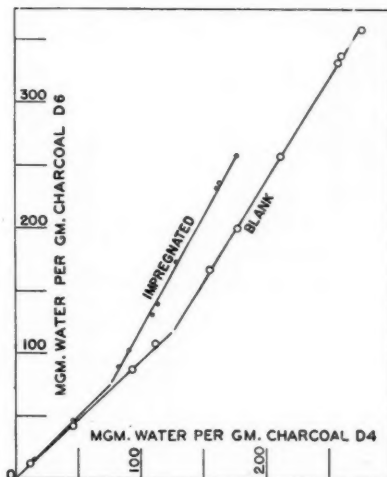


FIG. 7.

FIG. 6. Isotherms of isopiestic charges showing the effect of impregnating charcoals with benzoic acid on their water sorption. 25° C.

FIG. 7. Isotherms of isopiestic charges for the sorption of water by charcoals impregnated with benzoic acid and by the corresponding "blank" charcoals. 25° C.

Sorption of Methanol and Toluene

The isopiestic charges are tabulated in Tables IV and V and plotted as IIC's in Figs. 8 and 9. Samples of charcoal C were equilibrated with the

TABLE IV
ISOPIESTIC CHARGES OF METHANOL ON THE D-CHARCOALS AND CHARCOAL C AT 25° C.
(Mgm. methanol per gram charcoal)

D1	D2	D3	D4	D5	D6	D	C
*182	208	216	256	293	317	350	371
131	144	153	178	204	216	229	229
*183	202	205	240	285	316	357	380
136	150	160	190	218	231	246	251
158	175	187	229	270	296	331	354
129	142	149	171	191	198	206	208
100	106	108	112	117	116	113	112
82	86	87	87	87	84	81	83
63	64	64	62	60	58	56	65
111	121	125	136	145	146	145	144
*184	212	214	254	295	317	353	377
147	163	174	211	246	267	293	308

* Saturation.

TABLE V
ISOPIESTIC CHARGES OF TOLUENE ON THE D-CHARCOALS AND CHARCOAL C AT 25° C.
(Mgm. toluene per gram charcoal)

D1	D2	D3	D4	D5	D6	D	C
*109	144	192	253	310	344	398	414
105	138	184	242	295	326	374	386
102(.5)	133	177	230	280	308	352	361
101	131	173	222	269	296	336	345
** 95(.5)	123	161	204	243	264	291	298
** 87	112	144	178	205	219	233	239
** 84	108	137	167	191	202	212	220
** 77	100	125	150	165	175	179	189

* Saturation.

** Charcoal samples heated to 100° C. for one hour, then desorbed by evacuation while still hot.

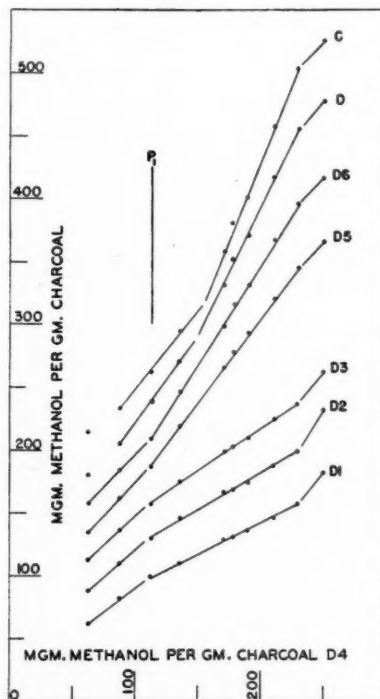


FIG. 8. Isotherms of isopiestic charges for the sorption of methanol by the activation series of charcoals. 25° C.

NOTE: For clarity the curves are separated by ordinate displacement. To obtain true ordinates:

Curve number	D1	D2	D3	D5	D6	D	C
Subtract from ordinate reading	0	25	50	75	100	125	150

activation series of charcoals since the former was the selected standard for isopiestic comparisons.* Here again the IIC's comprise linear sections and are simpler for any two of the charcoals *D1*–*D6* than for one of these compared with the unrelated charcoal *C*. Charcoal *D* behaves like an unrelated charcoal towards both methanol and toluene, as it did towards carbon tetrachloride.

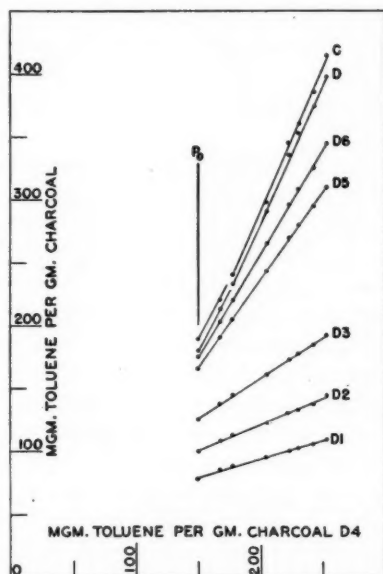


FIG. 9. Isotherms of isopiestic charges for the sorption of toluene by the activation series of charcoals. 25° C.

The IIC's for the sorption of toluene by charcoals *D1*–*D6* are the simplest for the four sorbates studied, being single straight lines from saturation pressure to a relative pressure (P_0 in Fig. 9) believed to be extremely small. This belief is based on the fact that the desorption of toluene by room temperature evacuation was very slow after the fourth set of isopiestic charges in Table V was obtained. The subsequent sets of isopiestic charges were determined by first heating the charged charcoals to 100° C. for one hour, then evacuating while still hot.

Discussion

Sorption of Water by the Activation Series

The pressure isotherms for water on the charcoal series resemble closely the desorption curves reported by Rakovsky (14) using blood charcoal, by Allmand and collaborators (1, 2, 3, 4) using wood and coconut shell charcoals,

* AUTHORS' NOTE: The pressure isotherms of methanol and toluene on the standard charcoal were determined in later experiments. These, and the pressure isotherms for the charcoal series computed from them, are more suitably reserved for a future report.

and by Coolidge (8) using coconut charcoal. The appreciable sorption at relative pressures below 0.3 reflects the presence of inorganic materials in the charcoals (2, 3, 4, 8), although the ash content was not determined. Water isotherms for an activation series of charcoals similar to ours have been reported by Fineman, Guest, and McIntosh (9). Although these were obtained by *adsorption* (condensation) rather than by *desorption*, the change in the curves as activation proceeds is roughly the same in both cases. The points of inflection of their curves are at approximately the same pressure, and at pressures below this value the activation process increased the activity of the charcoal very little.

The sorption of water by charcoals is often interpreted by the capillary condensation theory, in spite of serious anomalies reported by McBain, Porter, and Sessions (13). Fineman, Guest, and McIntosh, for example, have shown that the mean pore radius of a charcoal calculated from the water isotherm using the Cohan equation (7), assuming *adsorption* in annular rings, is in fair agreement with that computed from pore volume measurements using helium and mercury displacements plus surface area determinations by the method of Brunauer, Emmett, and Teller (6).

According to the capillary condensation hypothesis the capillaries of a given diameter will not sorb any water until a definite P/P_s is attained, at which P/P_s these capillaries become completely filled. The slope of the pressure isotherm at a certain P/P_s is therefore proportional to the amount of water that can be taken up by all the capillaries of the diameter corresponding to this P/P_s . Because of this correlation it is perhaps most convenient to define the "abundance of a given pore size" as being measured by the total volume of all capillaries of the given diameter, since the volume is directly proportional to the slope of the water isotherm. This definition will be used throughout the following discussion.

The most abundant pore size in the charcoal is that corresponding to the maximum slope of the pressure isotherm, i.e., to the point of inflection. The points of inflection for the activation series of charcoals occurred at approximately the same P/P_s , hence the most abundant pore size is not changed by activation from the state of charcoal $D1$ to that of D .

The lower lines of the IIC's for the charcoal series, corresponding to the P/P_s range 0 to 0.47, are concerned with condensation of water into capillaries smaller than the most abundant size. Some of the sorption encompassed by the lower lines, however, may be on the inorganic ash in the charcoal. The latter type of sorption should be independent of activation. The lower line for any two charcoals of the series approximates the 45° line, i.e., all the sorption over the P/P_s range 0 to 0.47 is practically independent of activation. Hence the abundance of all capillaries smaller than the most abundant size remains roughly unchanged during the activation process.

The upper linear portions of the IIC's corresponding to the P/P_s range 0.47 to unity, are concerned with capillaries larger than the most abundant size. For these larger capillaries it follows (5) that:

$$\frac{\Delta Q_{D1}}{\Delta P/P_s} = K_{D2} \cdot \frac{\Delta Q_{D2}}{\Delta P/P_s} = K_{D3} \cdot \frac{\Delta Q_{D3}}{\Delta P/P_s} = \dots \text{etc.}$$

where the K 's are constants independent of capillary size.

$$\text{As } \Delta P/P_s \rightarrow 0: \frac{\partial Q_{D1}}{\partial P/P_s} = K_{D2} \cdot \frac{\partial Q_{D2}}{\partial P/P_s} = K_{D3} \cdot \frac{\partial Q_{D3}}{\partial P/P_s} = \dots \text{etc.}$$

Replacing $\frac{\partial Q}{\partial P/P_s}$ by A , the abundance of the pore size corresponding to the P/P_s in question as heretofore defined, then:

$$A_{D1} = K_{D2} \cdot A_{D2} = K_{D3} \cdot A_{D3} = \dots \text{etc.}$$

Since charcoals $D2, D3, D4 \dots$ represent progressively longer activations of the initial charcoal $D1$, the above equations may be condensed to the general form: $A'_i = K \cdot A_i^0$, where A'_i is the abundance of the pore size i at Stage ' of the activation process, A_i^0 is the abundance of this pore size at the initial activation stage, and K is a constant independent of pore size and dependent upon the time of activation.

Thus the application of the capillary condensation hypothesis to the water sorption data yields the following picture of the activation process. There is a certain pore size which remains more abundant than any other size throughout the activation process. Considering any pore size smaller than the most abundant size, the rate of production is practically the same as the rate of enlargement, so that this pore size retains practically the same abundance throughout the activation process. For any pore size larger than the most abundant size, the rate of production continually exceeds the rate of enlargement and the abundance increases with activation. All such larger pore sizes, however, increase in abundance at the same relative rate, according to the condition: $A'_i = K \cdot A_i^0$.

Sorption by Charcoals Impregnated with Benzoic Acid

The charcoals impregnated with benzoic acid exhibit a marked decrease in the saturation charges for water. Applying the capillary condensation hypothesis, the saturation volume of water on an impregnated charcoal should be less than that on the corresponding blank charcoal by an amount equal to the volume of benzoic acid. Table VI shows that this is true for both the charcoals which were impregnated with benzoic acid. The volumes given in this table were calculated assuming the densities of water and benzoic acid on the charcoals to be the same as those of the pure substances.

The location of the benzoic acid in the charcoals may be gleaned from the IIC's of Fig. 6, which compare the impregnated charcoals with the corresponding blanks. The lowest linear portions of these IIC's resemble the lower portions of the IIC's for the activation series in that they cover the P/P_s range 0 to 0.45, practically the same range as the latter, and approximate

TABLE VI

VOLUMES OF SORBED WATER AND BENZOIC ACID ON CHARCOALS *D4* AND *D6*. 25° C.

P/P_s	Volume (cc.) on 100 gm. of charcoal:							
	<i>D4</i> impregnated			<i>D4</i> blank	<i>D6</i> impregnated			<i>D6</i> blank
	Benzoic acid	Water	Total	Water	Benzoic acid	Water	Total	Water
1	0.093	0.176	0.269	0.276	0.107	0.256	0.363	0.358
0.79	0.093	0.162	0.255	0.259	0.107	0.235	0.342	0.337
0.77	0.093	0.160	0.253	0.256	0.107	0.232	0.339	0.331
0.64	0.093	0.128	0.221	0.211	0.107	0.173	0.280	0.257
0.57	0.093	0.114	0.207	0.176	0.107	0.139	0.246	0.199
0.55	0.093	0.109	0.202	0.154	0.107	0.131	0.238	0.166
0.50	0.093	0.091	0.184	0.112	0.107	0.102	0.209	0.108
0.46	0.093	0.083	0.176	0.093	0.107	0.090	0.197	0.087
0.345	0.093	0.046	0.139	0.046	0.107	0.046	0.153	0.042
—	0.093	0.015	0.108	0.012	0.107	0.015	0.122	0.012

the 45° line. Thus impregnation with benzoic acid also has not appreciably changed the sorption by capillaries smaller than the most abundant size. Over the middle linear portions of the IIC's in Fig. 6, corresponding to the P/P_s range 0.45 to 0.65 for both charcoals, the blank charcoals exhibit considerably larger sorption than do the impregnated ones. Over this P/P_s range, impregnated charcoal *D4* has sorbed 0.091 ml. per gm. more water than blank *D4*, and impregnated *D6* has sorbed 0.105 ml. per gm. more than Blank *D6*. These values are in good agreement with the concentrations of benzoic acid on the impregnated charcoals viz., 0.093 and 0.107 ml. per gm. on *D4* and *D6* respectively. The benzoic acid is therefore all situated in pores which, before impregnation, were within the size range that filled with water at P/P_s values between 0.45 and 0.65.

Considering only this range of pore sizes, the linear IIC's of Fig. 6 may be described by the equation: $A_i^I = K^I \cdot A_i$, where A_i^I is the abundance of pore size i in the impregnated charcoal, A_i is its abundance in the blank charcoal, and K^I is a constant descriptive of the charcoal and independent of pore size. Thus the capillary condensation hypothesis leads to the following conclusions:

1. Benzoic acid has been taken up in such a manner that each pore size within the range in question is reduced in abundance by the same factor, K^I .
2. The abundance of pores larger or smaller than the size range in question has not been appreciably changed, i.e., no such larger or smaller pores have been created by the presence of benzoic acid. Consequently a fraction, $1 - K^I$, of each pore size within the range in question must have been filled or otherwise made inactive by the benzoic acid sorption.

These conclusions are inconceivable from the standpoint of any of the common theories applicable to the sorption of benzoic acid by charcoal. It may be stated, therefore, that the isopiestic water sorption data discredit the theory of capillary condensation.

Mechanism of Activation

The saturation charges for the four sorbates studied were converted to volumes using the density of the pure liquid. These saturation volumes, V_s , are plotted in Fig. 10, one sorbate against another with carbon tetrachloride as reference. They are linearly related for all four sorbates, i.e. if ΔV_s is the increase in sorption capacity during any given activation interval:

$$(\Delta V_s)_{\text{CCl}_4} = a \cdot (\Delta V_s)_{\text{water}} = b \cdot (\Delta V_s)_{\text{methanol}} = c \cdot (\Delta V_s)_{\text{toluene}}$$

In other words an increase in the activity of the charcoal towards any one of the sorbates is always accompanied by proportionate increases in its activity towards the other sorbates.

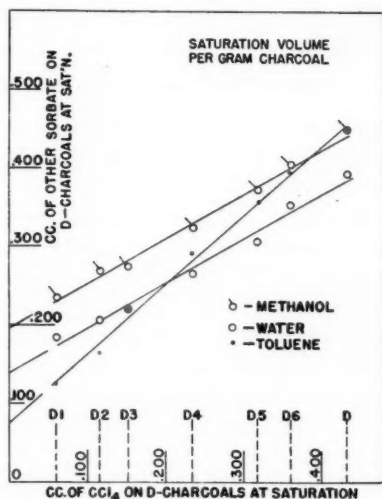


FIG. 10. Liquid volumes sorbed on the activation series of charcoals at saturation pressure.

Since the constants a , b , and c above are not unity, the new active centers created by the activation process do not sorb equal volumes of all four sorbate liquids at saturation. It would be expected, therefore, that the "Liquid Rule", which states that equal volumes of liquids are sorbed as the P/P_s of the vapor approaches unity, will not hold for activated charcoal at any stage in the activation process. The evidence in support of the Liquid Rule, summarized by McBain (12, pages 135-140), may be considered fortuitous, although one might expect the rule to hold when restricted to sorbates having similar molecular structures.

Fig. 10 has shown that any activation interval resulted in proportionate increases in charcoal activity for all four sorbates studied. Therefore the same active surfaces must be concerned with the sorption of each vapor. The IIC's supply information concerning the distribution of these active surfaces.

Fig. 3 showed that the IIC's for the sorption of water by the charcoal series each consisted of two straight lines. The lower lines all approached the 45° line, hence the activation process is concerned almost entirely with the upper lines of the IIC's. Similarly for the sorption of methanol and carbon tetrachloride, the activation process from stage D1 to stage D6 is concerned almost exclusively with the principal linear section of each IIC, since the lines above and/or below this section always approach the 45° line. Furthermore the principal lines cover practically the same P/P_s range independent of the activation state of the charcoal; this P/P_s range, however, is different for each sorbate. Thus the IIC's are single straight lines over the P/P_s range to which the charcoal becomes activated.

The mathematical significance of this, following the same reasoning as used above for the capillary condensation hypothesis but omitting all assumptions about the sorption mechanism, is given by the equation: $A_1 = k \cdot A_2$, where A , the activity at a given P/P_s , $\equiv \frac{\partial Q}{\partial P/P_s}$, the slope of the pressure isotherm at this P/P_s ; subscripts 1 and 2 refer to two stages of activation; and k is a constant independent of P/P_s but dependent upon the sorbate and the two activation stages considered.

This equation will be considered in the light of both homogeneous and heterogeneous surfaces, since the degree of heterogeneity in charcoals has never been firmly established. If, as assumed by the Langmuir theory of monomolecular adsorption, the active charcoal surface is homogeneous, then either all the pores have the same diameter and composition, or the surface inside the smaller pores has the same activity per unit area at any given P/P_s as does the surface inside the larger ones. In either case the above equation would apply, since the activity at any P/P_s would be directly proportional to the total active surface area.

If, on the other hand, the active charcoal surface is heterogeneous, the pores probably vary over a wide range of sizes and exhibit different activities per unit area at a given P/P_s . Local active centers may exist within the pores. Applying the above equation to such heterogeneous surfaces, the various types of active surfaces created by the activation process must be present in the charcoal in the same relative proportions at any stage of the activation process from D1 to D6.

Although these considerations have been derived from the data for water, carbon tetrachloride and methanol, they apply also to the toluene data over the whole P/P_s range of the measured IIC's. The IIC's for toluene, however, do not extrapolate even roughly to a single point on the 45° line. Thus the activation process has created active centers in the charcoal which sorb toluene below the P/P_s at which the IIC's become discontinuous. This P/P_s is even more minute than the value represented by P_0 in Fig. 9, which suggests that the surfaces active below the discontinuity pressure function by chemical combination rather than by adsorption.

The IIC's for toluene, carbon tetrachloride, and methanol exhibit an additional discontinuity in the case of charcoal *D*. For each sorbate this occurs near the low pressure end of the principal linear section of the IIC. When activation has progressed to the stage of charcoal *D*, therefore, the surfaces active at the lower pressures are being produced relatively more slowly. Since such surfaces would be associated primarily with the smaller pores, the activation process at this stage is producing new pores more slowly in comparison with the widening of existing pores. The additional discontinuity at the stage of charcoal *D* is not evident in the IIC's for water (Fig. 3.); the water data, however, are considered inconclusive with respect to the absence of this discontinuity.

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THE FORMATION AND PROPERTIES OF THREE-DIMENSIONAL POLYMERS

I. STATISTICS OF NETWORK POLYMERS¹

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Abstract

Theoretical treatments of the elastic and swelling properties of three-dimensional polymers are reviewed and the predicted influence of network structure discussed. An expression is obtained for the statistically most probable distribution of molecular weight for polymers terminated by chain transfer with a modifier. Depletion of modifier does not lead to a large increase in molecular heterogeneity. The formation of an insoluble fraction and the development of cyclic structures when such polymers are subjected to cross-linking conditions are treated by an application of the theory of gelation.

The peculiar mechanical properties of vulcanized rubber and certain other polymeric materials are generally ascribed to a three-dimensional network structure resulting from the presence of occasional cross-linkages between long chain-like molecules. Rubberlike elasticity has received extensive theoretical treatment, but experimental support for the theories has been comparatively meager. The course of a cross-linking reaction is difficult to follow since gelation intervenes after a small amount of reaction has occurred and makes analysis of the product difficult. Moreover, structural changes during vulcanization may be difficult to interpret if degradation accompanies cross-linking as a result of the rather drastic conditions generally employed.

It has been found in this laboratory that such difficulties are largely circumvented if the cross-linking reaction takes place in an emulsion of the polymer. In the investigations to be discussed in subsequent papers, the copolymer of butadiene and styrene (GR-S) was cross-linked at relatively low temperatures by addition of potassium persulphate to monomer-free latex.

In this first paper is presented an outline of relevant aspects of the statistical theory of three-dimensional polymers together with certain extensions of the theory that are required for interpretation of the experimental results.

Elasticity

It is now generally recognized that the retractive force in stretched rubber arises from thermal motions of the structural units rather than from attractive forces or deformation of valence angles. When rubber is stretched the long

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chains that make up its structure are forced into less random states. The deformation is therefore accompanied by a decrease of entropy. Measurements of the thermoelastic properties of rubber (1, 27, 29, 43) have shown that the major part of the retractive force is associated with the increase of entropy accompanying return to the more random (unstretched) state.

Proceeding from this viewpoint, a number of workers have derived expressions for the theoretical retractive force in terms of the elongation and the network structure. The "equation of state" for flexible polymer networks has been expressed (14, 21, 25, 36, 40) in the form:

$$\tau = \frac{\nu}{V} RT \left(\frac{l}{l_0} - \frac{l_0^2}{l^2} \right) \quad (1)$$

τ = tension (force per unit area of initial cross section),

R = gas constant,

T = absolute temperature,

l = stretched length,

l_0 = unstretched length,

$\frac{\nu}{V}$ is a proportionality constant characteristic of the rubber sample and dependent on structure. It will henceforth be called the "network activity."

The deduced dependence of retractive force on temperature and elongation agrees with experimental thermoelastic properties (1, 27, 29) and stress-strain curves (1, 9, 29, 37, 44) for various rubberlike polymers. On the other hand elasticity theories do not agree on the exact dependence of the proportionality constant $\frac{\nu}{V}$ on network structure. In several of the theories this quantity is proportional to the number of "chains" per unit volume where the "chain" is defined as the part of a molecule extending from one cross-linkage to the next. For an ideal network formed from indefinitely long molecules, the number of chains is identical with the number of cross-linked monomer units or equal to twice the number of cross-linkages. If a fraction ρ of the structural units is involved in cross-linkages, the concentration of chains (moles per cubic centimeter) is $\frac{d}{M_0} \rho$ and the theoretical relation between network activity and degree of cross-linking is given by:

$$\frac{\nu}{V} = g \frac{d}{M_0} \rho \quad (2)$$

d = density of the polymer (grams per cubic centimeter),

M_0 = molecular weight of the structural unit.

The proportionality constant, g , is unity in the theories developed by Wall (39, 40, 41), Treloar (36), and Flory and Rehner (14). Kuhn (24, 25) believes

that vulcanized rubber contains "steric junction points" in addition to chemical cross-linkages, and has arrived at a theoretical value of $\frac{7}{3}$ for g . James and Guth (22) conclude that g should be above $1/2$.

Flory has taken into account the molecular weight of the polymer before cross-linking (9, 11). Each "primary molecule" is considered to give rise to two inactive terminal chains in the vulcanizate, thereby leading to an "effective" degree of cross-linking of $\rho - \frac{2}{\bar{y}_n}$ where \bar{y}_n is the number average degree of polymerization prior to cross-linking. Equation (2) may then be modified to:

$$\frac{\nu}{V} = g \frac{d}{M_0} \left(\rho - \frac{2}{\bar{y}_n} \right). \quad (3)$$

Experiments with close-cut fractions of butyl rubber confirmed the validity of this correction for initial molecular weight, but failed to support the theoretical proportionality between network activity and degree of cross-linking (9, 11). Experimental values of g were 3.3 for $\rho = 1.6 \times 10^{-3}$ and 2.1 for $\rho = 2.8 \times 10^{-3}$. Flory has suggested that the discrepancy between theory and experiment results from entanglements within the network which restrict chain configurations and so augment the retractive force.

Swelling

Polymers possessing a network structure swell when placed in suitable liquids. Flory and Rehner (15) have developed a thermodynamic treatment of the swelling phenomenon which relates equilibrium swelling volume and network activity $\left(\frac{\nu}{V} \right)$:

$$\frac{\nu}{V} = \frac{\ln(1 - v_2) + v_2 + \mu_g v_2^2}{-V_1 v_2^{1/3}}, \quad (4)$$

v_2 = volume fraction of polymer in the swollen gel in equilibrium with pure solvent; i.e., the reciprocal of the "swelling volume" (ratio of the volumes of swollen and dried gel),

μ_g = solvent-polymer interaction coefficient (10, 19),

V_1 = molar volume of solvent.

For large swelling (v_2 small), Equation (4) reduces to the approximate expression

$$\frac{\nu}{V} \doteq \frac{(1 - 2\mu_g) v_2^{5/3}}{2 V_1}. \quad (5)$$

Combining Equations (1) and (5), the relation between tension and equilibrium swelling volume is:

$$\tau \doteq \frac{RT \left(\frac{l}{l_0} - \frac{l_0^2}{l^2} \right) (1 - 2\mu_g) v_2^{5/3}}{2 V_1}, \quad (6)$$

i.e., the tension at a given elongation should be inversely proportional to the 5/3 power of the swelling volume. Butyl rubber swollen in cyclohexane has been shown to conform to this relation (9).

Primary Molecular Size Distribution

Prior to cross-linking, polymeric molecules possess a distribution of molecular size, which is the statistical result of the random occurrence of termination steps during chain growth. If the probability that a growing molecule adds an additional monomer unit is represented by p then the distribution of primary molecular size of the resulting polymer (4, 31) is given by:

$$W_y = y (1 - p)^2 p^{y-1}, \quad (7)$$

W_y = weight fraction of species containing y structural units.

The above distribution has been discussed by several workers (4, 18, 30, 31) who have shown that the following relations exist.

The "number average" value of y

$$\bar{y}_n = \frac{1}{1 - p}.$$

The "weight average" value of y

$$\bar{y}_w = \frac{1 + p}{1 - p}.$$

The "heterogeneity index"

$$\frac{\bar{y}_w}{\bar{y}_n} = 1 + p \doteq 2,$$

since if a high polymer is to result p must be close to unity.

The "viscosity heterogeneity index"

$$\frac{\bar{y}_v}{\bar{y}_n} \doteq \{\Gamma (2 + a)\}^{1/a},$$

where a is the empirical coefficient (8, 20) in the relation between intrinsic viscosity (η) and degree of polymerization*

$$(\eta) = K \bar{y}_v^a.$$

The foregoing relations will now be employed to discuss the primary molecular size distribution in polymers such as GR-S formed in the presence of a chain transfer agent (modifier). Since abundant evidence (23, 32, 33, 42) indicates that here the main termination mechanism is transfer with the modifier, the probability (or rate) of termination relative to propagation may

* For GR-S dissolved in benzene or toluene (16) a has the value of 0.67, and the theoretical viscosity heterogeneity index at low conversion is about 1.85. Measurements by Harris and Kolthoff with GR-S of 5% conversion give an average value of 1.84 ± 0.09 (17), thereby providing partial confirmation for the distribution represented by Equation (7).

be taken equal to the rate of modifier disappearance relative to conversion. The latter is generally first order with respect to conversion up to at least 50% yield (3, 28), i.e.,

$$\frac{1-p}{p} = -\frac{dR}{d\alpha} = rR \quad (8)$$

R = modifier concentration (as moles per mole of initial monomer),

α = fractional conversion,

r = "regulating index" (3).

Since p is very close to unity, the above equation may be replaced by:

$$1-p \doteq rR. \quad (9)$$

In general p varies as conversion proceeds. The cumulative distribution at conversion α_1 is then

$$\begin{aligned} W_{y\alpha_1} &= \frac{1}{\alpha_1} \int_0^{\alpha_1} W_y d\alpha \\ &= \frac{1}{\alpha_1} \int_0^{\alpha_1} y (1-p)^2 p^{y-1} d\alpha. \end{aligned}$$

From Equations (8) and (9)

$$d\alpha = \frac{dp}{r(1-p)}.$$

$$\begin{aligned} \text{Hence } W_{y\alpha_1} &= \frac{1}{r\alpha_1} \int_{p_0}^{p_1} y (1-p) p^{y-1} dp \\ &= \frac{1}{r\alpha_1} \left\{ p_1^y \left(1 - \frac{y}{y+1} p_1 \right) - p_0^y \left(1 - \frac{y}{y+1} p_0 \right) \right\}. \quad (10) \end{aligned}$$

p_0 and p_1 are the values of the parameter at conversions zero and α_1 , respectively.

The "number average" value of y at conversion α_1 is given by:

$$\begin{aligned} \bar{y}_{n\alpha_1} &= \frac{\text{Moles of monomer polymerized}}{\text{Moles of modifier consumed}}, \\ &= \frac{\alpha_1}{R_0 - R_1}. \quad (11) \end{aligned}$$

R_0 and R_1 are the modifier concentrations (as defined above) initially and at conversion α_1 , respectively.

Integrating Equation (8)

$$R_1 = R_0 e^{-r\alpha_1}. \quad (12)$$

$$\bar{y}_{n\alpha_1} = \frac{\alpha_1}{R_0 (1 - e^{-r\alpha_1})}. \quad (13)$$

The "weight average" value of y at conversion α_1 is given by:

$$\begin{aligned}\bar{y}_{w\alpha_1} &= \frac{1}{\alpha_1} \int_0^{\alpha_1} \bar{y}_w d\alpha \\ &= \frac{2}{r\alpha_1} \int_{p_0}^{p_1} \frac{dp}{(1-p)^2} \\ &= \frac{2}{r\alpha_1} \left(\frac{1}{1-p_1} - \frac{1}{1-p_0} \right) \\ &= \frac{2}{r^2\alpha_1} \left(\frac{1}{R_1} - \frac{1}{R_0} \right) \\ &= \frac{2}{r^2\alpha_1 R_0} (e^{r\alpha_1} - 1) .\end{aligned}$$

Hence the heterogeneity index at conversion α_1 is given by:

$$\frac{\bar{y}_{w\alpha_1}}{\bar{y}_{n\alpha_1}} = \frac{2}{(r\alpha_1)^2} (e^{r\alpha_1} - 1) (1 - e^{-r\alpha_1}) . \quad (14)$$

The heterogeneity index is seen to depend only on the value of the product $r\alpha_1$ and to be independent of the magnitude of the average degree of polymerization. This implies (cf. Equation (12)) that the heterogeneity index depends only on the fractional depletion of modifier, and not on the amount (or type) of modifier used.

By means of Equations (12) and (14) it can be shown that at the point of 50% depletion of modifier the heterogeneity index rises only to 2.08. With further depletion the heterogeneity index increases somewhat more rapidly, reaching the value 3.06 when 90% depletion has taken place.

The effect of modifier depletion on the cumulative primary distribution is illustrated further by the following calculations. A value of 0.999 is taken for p_0 corresponding to a number average degree of polymerization \bar{y}_n of 1000 units for the polymer formed initially. The distributions (W_y) for the polymer formed up to 50 and 90% depletion of modifier were calculated by means of Equation (10) with p_1 equal to 0.9995 and 0.9999, respectively. These distributions are shown in Fig. 1. For comparison the increment distributions (Equation (7)) for the same number average primary molecular size are shown ($p = 0.99928$ and 0.99961). The latter curves represent the distributions that would have resulted from 50 and 90% depletion of modifier, had the modifier and monomer been used up at the same relative rate. It is seen that up to at least 50% depletion of modifier the *form* of the distribution is distorted only slightly. Further distortion is found at 90% depletion but

even for this extent of modifier disappearance the increase of heterogeneity in the size distribution of the primary molecules is not marked.*

In the foregoing discussion, no mention is made of the possibility of branching reactions, such as may occur as a result of chain transfer with a hydrogen atom on the body of another molecule (2, 5, 26). Although such branching

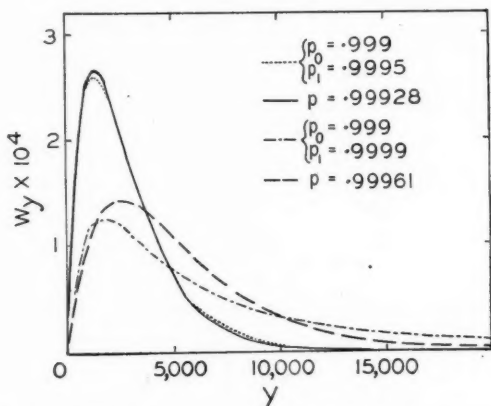


FIG. 1. Typical cumulative distributions for 50% and 90% depletion of modifier.

reactions may distort the primary molecular size distribution somewhat, they do not alter the 1 : 1 ratio of modifier fragments to polymer molecules, nor do they interfere in any way in the application of the statistical theory of gelation (35).

Gel Formation

The theoretical aspects of cross-linking have been examined statistically by Flory (6, 7, 12) and Stockmayer (34, 35). As polymer molecules are bonded together, large structures are gradually built up, a process that eventually results in the formation of "infinite networks" pervading the entire volume. Such networks are insoluble in normal solvents for the polymer and constitute the gel fraction.

On the assumption that cross-linking is random and that intramolecular connections within the sol fraction may be neglected, Flory has derived equations that, when applied to specific initial distributions, relate the weight fraction of gel and other quantities of interest to the degree of cross-linking (12). The degree of cross-linking, designated by ρ is defined as the fraction of structural units (monomer) involved in cross-linkages. In obtaining the various relations Flory has employed a quantity ϕ_s defined as the probability that a non-cross-linked structural unit selected at random is part of the sol fraction. The weight fractions of sol and gel are designated by W_s and W_g ,

* The measured heterogeneity of the actual molecular size distribution is generally found to exceed estimates made in this way, probably as a result of cross-linking during polymerization (13, 38). The primary distribution, by definition, is unaffected by such cross-linking reactions.

respectively. The statistical relations between ρ , W_s , ϕ_s , and the initial primary molecular size distribution, W_y , are given by:

$$\frac{W_s}{\phi_s} \doteq 1 - \rho (1 - W_s) \quad (15)$$

$$W_s = \sum_{y=1}^{\infty} W_y \left(\frac{W_s}{\phi_s} \right)^y. \quad (16)$$

For a given form of primary distribution an explicit relation exists between the weight fraction of gel, and the average number of cross-linked units per primary molecule $\rho \bar{y}_n$. Methods of calculating this relation for a polymer of homogeneous molecular weight and for the "increment" distribution [Equation (7)] have been given by Flory (12). The results are plotted in Fig. 2.

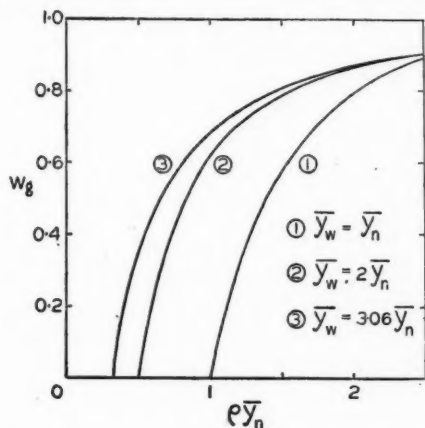


FIG. 2. Statistical relation between weight fraction of gel and average number of cross-linked units per primary molecule; for (1) homogeneous polymer, (2) increment, and (3) cumulative distributions.

The relation for the cumulative distribution may be found by substituting Equation (10) in Equation (16) and evaluating the summations. The final result is:

$$W_s = \frac{1}{r \alpha_1} \left\{ \frac{(1 - p_1) p_1 \frac{W_s}{\phi_s}}{1 - p_1 \frac{W_s}{\phi_s}} - \frac{(1 - p_0) p_0 \frac{W_s}{\phi_s}}{1 - p_0 \frac{W_s}{\phi_s}} \right. \\ \left. + \frac{1}{\frac{W_s}{\phi_s}} \left[\ln \frac{1 - p_0 \frac{W_s}{\phi_s}}{1 - p_1 \frac{W_s}{\phi_s}} \right] + p_0 - p_1 \right\}$$

Calculations were made for the specific case of 90% modifier depletion, i.e.,

$$\frac{1 - p_0}{1 - p_1} = \frac{R_0}{R_1} = 10$$

$$r \alpha_1 = 2.303$$

$$y_w = 3.06 y_n$$

Values of 0.999 and 0.9999 were used for p_0 and p_1 and the values of W_s for arbitrary values of $\frac{W_s}{\phi_s}$ deduced. Substitution of these values in Equation (15) yielded values of ρ from which the quantity $\rho \bar{y}_n$ was then obtained. Curve (3) of Fig. 2 shows the weight fraction of gel vs. $\rho \bar{y}_n$ for the distribution resulting from 90% depletion of modifier.

The course of gelation is seen to be similar for the three distributions considered. The gel fraction appears when ρ exceeds $\frac{1}{\bar{y}_w}$ (35) and then increases rapidly with further cross-linking, approaching unity asymptotically.

The constitution of the gel fraction itself will now be considered. The degree of cross-linking of the gel fraction, ρ'' , is related (12) to ρ , the degree of cross-linking of the aggregate of sol and gel, by the equation:

$$\rho'' = \rho (2 - W_g)$$

The number average degree of polymerization \bar{y}_n of the primary molecules in the sol fraction is given by:

$$\bar{y}_n = \frac{W_s}{\sum_{v=1}^{\infty} \frac{W_v}{y} \left(\frac{W_s}{\theta_s} \right)^v} \quad (17)$$

The corresponding number average degree of polymerization \bar{y}_n'' of the primary molecules in the gel fraction can be obtained by difference. The total number of primary molecules per structural unit is $\frac{1}{\bar{y}_n}$. If a weight fraction of gel, W_g , is present, the number of primary molecules in the gel is $\frac{W_g}{\bar{y}_n''}$ and that in the sol $\frac{1 - W_g}{\bar{y}_n}$. The value of \bar{y}_n'' is determined by:

$$\frac{W_g}{\bar{y}_n''} = \frac{1}{\bar{y}_n} - \frac{1 - W_g}{\bar{y}_n}$$

Consequently if the primary distribution is known and the gel fraction has been measured, the constitution of the gel with respect to degree of cross-linking and primary molecular size may be deduced.

Of particular interest from the viewpoint of elasticity theory is the degree of *cyclic* cross-linking, or the number of "effective" chains per structural unit. It will be recalled from the considerations leading to Equation (3) that if all

of the molecules have been linked to the network the number of "effective" chains per structural unit is $\rho - \frac{2}{\bar{y}_n}$. If, however, the degree of cross-linking is sufficiently low that an appreciable sol fraction results, attention must be confined to the gel fraction, since soluble molecules make no permanent contribution to the retractive force. Consequently the number of "effective" chains per structural unit is $\rho'' - \frac{2}{\bar{y}_n''}$ and the number of "effective" chains per primary molecule is $\bar{y}_n \left(\rho'' - \frac{2}{\bar{y}_n''} \right)$.

The function $\bar{y}_n \left(\rho'' - \frac{2}{\bar{y}_n''} \right)$ may be calculated for various forms of the initial primary distribution. This calculation has been made for the three cases considered above; viz., the homogeneous, increment, and cumulative distributions. The summation involved in Equation (17) and the remaining calculations were made in a manner exactly analogous to that employed in deducing the relation between W_g and $\rho\bar{y}_n$.

In Fig. 3 the function $\bar{y}_n \left(\rho'' - \frac{2}{\bar{y}_n''} \right)$ is plotted against $\rho\bar{y}_n$ for the three distributions considered (The cumulative distribution employed corresponds

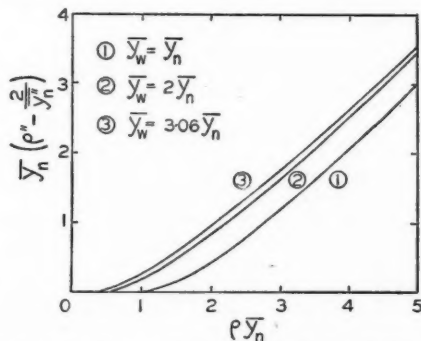


FIG. 3. Statistical relation between the number of effective chains and the average number of cross-linked units per primary molecule for (1) homogeneous polymer, (2) increment, and (3) cumulative distributions.

to 90% modifier depletion). It is seen that after gelation begins, "cyclic" cross-linkages form at an accelerating rate with further cross-linking. In general the relation of the various distributions to one another is similar to that found for the gel fraction (Fig. 2).

This relation is demonstrated further in Fig. 4, where $\bar{y}_n \left(\rho'' - \frac{2}{\bar{y}_n''} \right)$ is plotted against the corresponding sol fraction. Over a considerable range of solubility the measured gel fraction is associated with about the same average

number of "effective" chains per primary molecule for all of the distributions considered.

The statistical relations discussed above will be employed in a subsequent paper dealing with the formation and properties of butadiene-styrene copolymer networks.

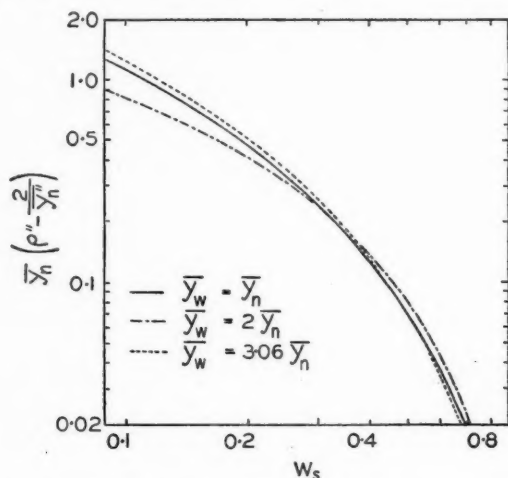


FIG. 4. Statistical relation between the number of effective chains per primary molecule and the weight fraction of sol for homogeneous polymer, increment, and cumulative distributions (log-log plot).

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THE FORMATION AND PROPERTIES OF THREE-DIMENSIONAL POLYMERS

II. NETWORK FORMATION¹

By J. BARDWELL² AND C. A. WINKLER

Abstract

Addition of potassium persulphate to a latex leads to cross-linking with typical diene polymers but has little effect on polystyrene. The rate of cross-linking is directly proportional to the persulphate concentration. The activation energy is 26,900 cal. The rate depends on latex particle size and is affected by the presence of other reagents. The course of gelation supports the predictions of the statistical theory of random cross-linking.

Introduction

The development of three-dimensional network structures when cross-linkages are introduced between polymer molecules has been subjected to detailed statistical analysis (6, 16). On the other hand experimental study of the cross-linking processes that occur in conventional vulcanizations is hampered by the reaction conditions employed and by the variety of side reactions encountered. The theory of network formation is therefore at a more advanced stage of development than experiment.

A simpler method of cross-linking polymer molecules has been developed in this laboratory. The addition of potassium persulphate to an emulsion of polymer (e.g., a latex) leads to the formation of insoluble three-dimensional structures.

Experimental

Cross-linking Reaction

The polymer used in most of the investigations described below was the well known copolymer of butadiene and styrene (GR-S), in the form of a monomer-free latex prepared by Polymer Corporation, Sarnia. The modifier used was commercial dodecyl mercaptan and the conversion was 70%.

To promote cross-linking, a solution of potassium persulphate buffered with an equimolar mixture of sodium carbonate and sodium bicarbonate was added to the latex, the final mixture having the following composition:

Polymer (GR-S)	5.0%
Potassium persulphate	2.5%
Buffer (sodium carbonate - sodium bicarbonate)	1.5%

After thorough mixing, aliquots of 25 cc. were transferred to one-ounce bottles. Nitrogen was bubbled through the reaction mixture for 30 secs.,

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after which the bottle was capped tightly and immersed in a water bath at $50.0 \pm 0.5^\circ \text{C}$. After suitable intervals the reaction was stopped by coagulating the polymer in rapidly stirring butanol containing 0.05% phenyl- β -naphthylamine antioxidant (P.B.N.A.). The coagulum was washed with butanol, 2% P.B.N.A. was added, and the polymer was dried for 12 hr. at 80°C . in a vacuum oven.

Solubility and Swelling

Weighed fragments of the dried polymer were placed in small screen cages and extracted for 48 hr. in toluene containing 0.05% P.B.N.A. The cage containing the swollen gel was then placed on a pad of filter paper in a small closed container and allowed to drain for five minutes. After its weight was determined, the swollen gel was dried to constant weight and the gel fraction and "swelling volume" calculated, using the values of 0.93 and 0.86 for the densities of GR-S and toluene respectively. The solubility was corrected for the small amount of nonpolymer components extractable in ethanol-toluene azeotrope containing 10% water (11).

Values of gel fraction and swelling volume determined in this way depend somewhat on the extent to which the polymer is dried. Unless the coagulum is thoroughly dried, colloidal dispersion of "microgel" may interfere, leading to low values for the gel fraction (15). This effect is illustrated in Fig. 1, which shows that the measured gel fraction increases as the time of drying is increased,

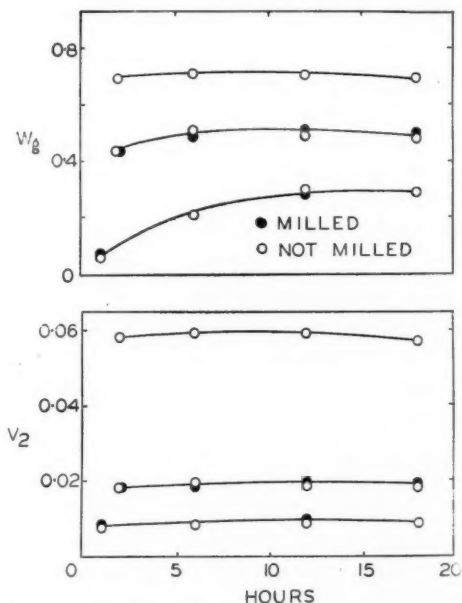


FIG. 1. Effect of heating at 80°C . in a vacuum oven, on the measured gel fraction, W_g , and reciprocal swelling volume, v_2 .

particularly when the insoluble fraction is small. The effect of drying has been thoroughly investigated by Medalia and Kolthoff (15), who have shown that heating for 12 hr. at 80° C. in a vacuum oven is effective in minimizing colloidal dispersion of "microgel" with GR-S polymers. The results shown in Fig. 1 support this conclusion. Mechanical mixing (milling) of the coagulum prior to heating does not appear to have any significant effect on the values obtained.

Thorough drying of the polymer has the additional advantage that the values obtained are insensitive to variations in the time and temperature of extraction. The results shown in Fig. 2 indicate that the rate of extraction does not depend

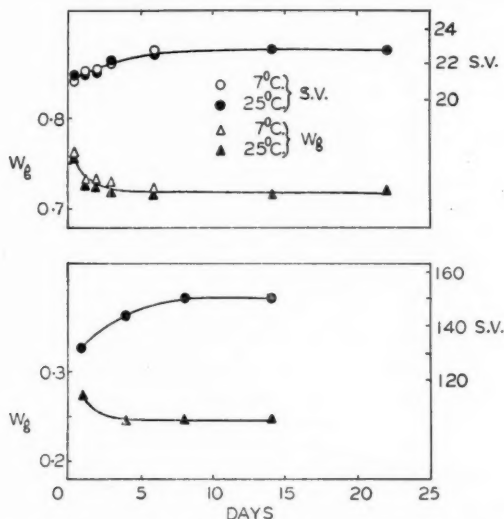


FIG. 2. Effect of prolonged extraction on the measured gel fraction, W_g , and swelling volume, S.V.

markedly on temperature between 7 and 25° C., and that removal of soluble polymer is virtually complete after 48 hr. The slow increase of swelling during the next few days is believed to result from oxidative breakdown (7, p. 179); the value after 48 hr. may then be accepted as approximating the equilibrium swelling volume.

Baker has shown that several solvents give the same value of gel fraction with GR-S polymers (1). This conclusion was verified and extended by extracting portions of a partially soluble polymer with toluene, benzene, xylene, nitrobenzene, chlorobenzene, chloroform, carbon tetrachloride, ethyl ether, and methyl amyl ketone. Despite the diverse chemical nature of the solvents employed, the measured gel fraction showed a variation of less than 2%.

The foregoing results indicate that the method used for determining solubility and swelling is suitable for characterizing cross-linked polymers.

Results and Discussion

When potassium persulphate is added to GR-S latex, the polymer undergoes a progressive loss of solubility. The swelling volume of the gel also decreases. Typical results are shown in Fig. 3, in which the gel fraction (W_g) and recip-

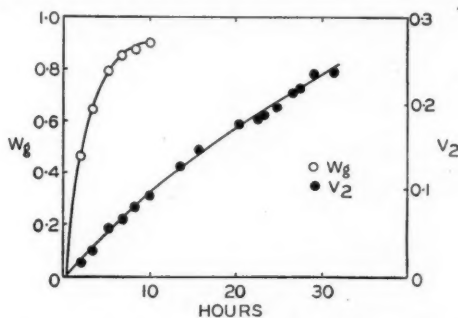


FIG. 3. Rate of increase of gel fraction and reciprocal swelling volume.

rocal swelling volume (v_2) are plotted vs. time of reaction. Further evidence of the cross-linking reaction is found in the increasing hardness of the dried coagulum. Several other features of this reaction were investigated, as follows.

Viscosity of Soluble Polymer

The viscosity of the solution remaining after removal of the gel fraction was measured in an Ubbelohde viscometer at 25° C., and the intrinsic viscosity $[\eta]$ determined by extrapolating to zero concentration. The results given in Table I show that the molecular weight of the sol fraction decreases as gelation proceeds. This result is in agreement with the statistical theory of random cross-linking (6).

TABLE I

INTRINSIC VISCOSITY OF SOLUBLE FRACTION

Gel fraction	$[\eta]$
0	2.09
0.29	1.60
0.44	1.31
0.70	0.72
0.81	0.25

Decomposition of Persulphate

Green and Masson have shown that the decomposition of persulphuric acid or its salts in aqueous solution is generally first order, the rate constant depending slightly on the composition of the reaction medium (10). The rate

constant for persulphate decomposition at 50° C. in latex buffered at a pH of about 9 was determined from measurements of residual persulphate by the method of Kolthoff *et al.* (12). Control experiments showed that the presence of a small amount of latex did not interfere with the analysis and did not greatly affect the rate of persulphate decomposition. The results shown in Fig. 4 yield a first order velocity constant, k , of 0.0084 hr.⁻¹; i.e., the half-life of the persulphate ion at 50° C. is about 83 hr., a satisfactorily long period.

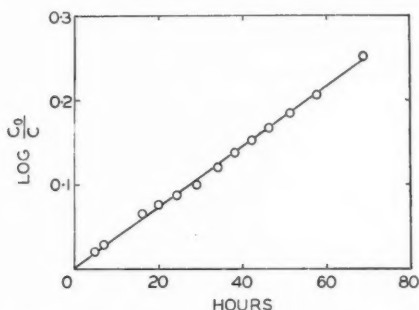


FIG. 4. First order decomposition of potassium persulphate in buffered latex at 50° C.

The Energy of Activation

The rate of cross-linking was determined at four temperatures ranging from 30 to 76° C., and expressed in arbitrary units based on the time required to produce a given gel fraction. The data shown in Table II yield an energy of activation of about 26,900 cal., a value quite close to that of 26,000 cal. obtained by Eager and Winkler for the decomposition of potassium persulphate in aqueous 80% acetic acid (5).

TABLE II
EFFECT OF TEMPERATURE ON RATE OF CROSS-LINKING

Temperature, °C.	Rate of cross-linking (arbitrary units)
30.1	1
50.0	18
60.0	65
76.0	370

Unbuffered System

When no buffer is included, the course of the reaction is complicated by increasing acidity which results from the decomposition of persulphate. The most obvious result of the fall of pH is agglomeration of the latex particles, revealed by loss of Tyndall effect and eventually by coagulation.

The pH of the reaction mixture was measured with a glass electrode, and particle size of the latex by the method of light scattering (2, 4). For the latter measurements the reaction mixture was diluted to suitable concentrations with dilute (0.06%) soap solution and the turbidity measured with a Beckman spectrophotometer. Particle diameters were calculated from the turbidity-concentration ratio at infinite dilution (2).

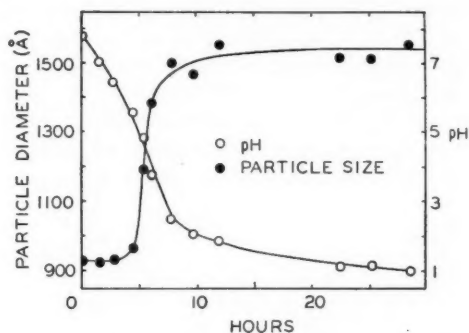


FIG. 5. Change of pH and particle size with progress of reaction (unbuffered).

In Fig. 5, pH and particle diameter are plotted against time of reaction. It is interesting to note that no appreciable agglomeration of the latex particles occurs until the pH falls to about 6. Average particle diameter then rises sharply from about 900 Å to about 1500 Å after which little further change occurs. In the latter region however, the emulsion appears to be metastable; a coagulum separates when the mixture is agitated.

When the reaction mixture is adequately buffered, practically no agglomeration occurs for several days. The results given in Table III show that changes of pH and particle size are very slow when the usual amount of buffer is included.

TABLE III
CHANGE OF pH AND PARTICLE SIZE IN BUFFERED REACTION MIXTURE
AT 50.0° C.

Reaction mixture		
Polymer (GR-S)		5.0%
Potassium persulphate		2.5%
Buffer (sodium carbonate - sodium bicarbonate)		1.5%
Reaction time, hr.	pH	Particle diameter, Å
0	9.7	930
12.2	9.5	950
24.0	9.2	975
48.1	8.4	1030

Factors affecting the Rate of Cross-linking

At a given concentration of polymer and potassium persulphate, the rate of cross-linking is affected by the presence of other materials. In Table IV are shown the effects of various added reagents on the rate of insolubilization.

TABLE IV
EFFECT OF VARIOUS REAGENTS ON THE RATE OF INSOLUBILIZATION AT 50° C.

<i>Reaction mixture</i>		
Polymer (GR-S)		13%
Potassium persulphate		1.5%
Buffer (sodium carbonate - sodium bicarbonate)		0.9%
Reaction time—16 hr.		
Reagent added	Gel fraction	Reciprocal swelling volume
None	0.836	0.0636
0.1% silver nitrate	0.880	0.0752
0.8% <i>n</i> -dodecyl mercaptan; bottle flushed with nitrogen	0.919	0.0980
0.8% <i>n</i> -dodecyl mercaptan; bottle flushed with oxygen	0.787	0.0566
8% <i>n</i> -dodecyl mercaptan; bottle flushed with nitrogen	0.785	0.0406
16% toluene	0.457	0.0108
0.08% phenyl- β -naphthylamine	0.393	0.0119
0.8% hydroquinone	0.145	0.0058

It is seen that small amounts of silver ion and of *n*-dodecyl mercaptan have an accelerating effect on the cross-linking reaction. The action of silver ion as a "catalyst" for oxidations involving persulphate (8, p. 1118) and the role of traces of mercaptans as "promoters" in the polymerization of butadiene (13) are well known. Similarly the use of phenyl- β -naphthylamine as an antioxidant and of hydroquinone as a "shortstop" in polymerizations is widespread, and their retarding effect on the cross-linking reaction is not unexpected. The retardation caused by relatively large amounts of *n*-dodecyl mercaptan and of toluene may be due to chain transfer activity or merely to dilution of the polymer. The apparent retarding effect of traces of *n*-dodecyl mercaptan in the presence of oxygen may be due to a competing scission reaction. Some evidence for such a reaction with soluble polymer has been found by Kolthoff and Stenberg (14). When no mercaptan was added, however, the rate of insolubilization was found to be unaffected by the presence of oxygen. The addition of soap to the latex was likewise found to be without effect.

Some evidence was found to show that the rate of insolubilization depended on the particle size of the latex. When the reaction mixture was cooled and subjected to prolonged centrifuging, some of the larger particles collected at the surface. Comparison with the remaining latex indicated that the polymer within these larger particles had become cross-linked at a rate that was about 20% smaller than the rate of cross-linking of the remainder. This result

suggests that the *initial* activation of the polymer takes place only at the polymer-water interface.

At a given concentration of polymer the rate of cross-linking was found to increase as the initial concentration of persulphate was increased. The effect of persulphate concentration was investigated quantitatively by interpreting the resulting gel fraction through the statistical theory of gelation (3, 6). For this purpose the form of the primary molecular size distribution of the polymer used was assumed to be given to an adequate approximation by the theoretical cumulative distribution (3, Equation 10), corresponding to 90% modifier depletion. The theoretical course of gelation for this distribution has been calculated (3, Curve 3 of Fig. 2). By means of this relation the rates of cross-linking for various initial concentrations of potassium persulphate were calculated from the observed increase of gel fraction. The

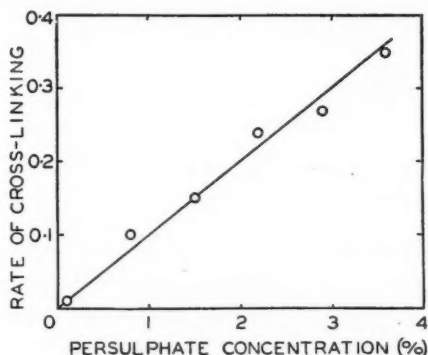


FIG. 6. Effect of initial persulphate concentration on the rate of cross-linking.

results shown in Fig. 6 demonstrate that the rate of cross-linking is directly proportional to the concentration of persulphate, i.e.,

$$\frac{d\rho}{dt} = k_z c, \quad (1)$$

ρ = fraction of structural units involved in cross-linkages,

c = concentration of persulphate,

k_z = cross-linking velocity "constant"

for the reaction conditions employed (polymer concentration, latex particle size, etc.)

Since the decomposition of persulphate is first order (Fig. 4) the concentration at time t is given by

$$c = c_0 e^{-kt}$$

Substituting for c in Equation (1) and integrating

$$\rho = \rho_0 + k_z c_0 \left(\frac{1 - e^{-kt}}{k} \right). \quad (2)$$

ρ_0 and c_0 are the values of ρ and c initially.

On this basis it is to be expected that, as the time of reaction increases, the degree of cross-linking of the polymer will be linear with $\frac{1 - e^{-kt}}{k}$, or to a first approximation with t since k is small at 50° C.

The results shown in Fig. 3 provide excellent confirmation of this prediction. The average number of cross-linked units per primary molecule ($\rho\bar{y}_n$) was

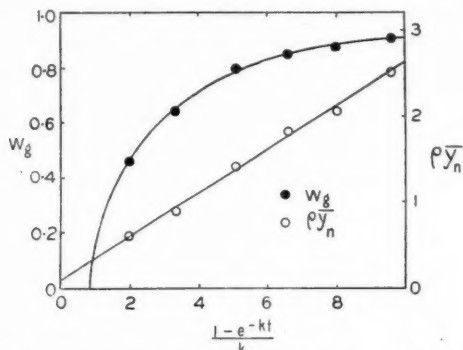


FIG. 7. Weight fraction of gel and average number of cross-linked units per primary molecule, vs. $\frac{1 - e^{-kt}}{k}$ (Equation 2).

calculated from the observed gel fraction and is shown in Fig. 7 as a function of $\frac{1 - e^{-kt}}{k}$ computed from the reaction time with $k = 0.0084 \text{ hr.}^{-1}$. The relation is linear and can be expressed by the equation:

$$\rho\bar{y}_n = 0.09 + 0.254 \left(\frac{1 - e^{-kt}}{k} \right). \quad (3)$$

A plot of $\rho\bar{y}_n$ vs. time is nearly as satisfactory since over this interval the concentration of persulphate changes by less than 10%. The linearity of these plots shows that the course of gelation predicted by statistical theory is in harmony with the experimental results for the cross-linking reaction under investigation.

Extrapolation of the line in Fig. 7 to zero time permits estimation of the degree of cross-linking of the initial (soluble) polymer. Moreover, a simple method now becomes available for calculating the degree of cross-linking of the virtually insoluble polymers resulting from longer reaction periods. The determination of these quantities by direct experiment is usually difficult.

For the polymer involved here, the value of \bar{y}_n , the average primary chain length, may be estimated from modifier consumption to be of the order of 800 units. Comparing Equations (2) and (3), the deduced value of $k_x c_0$ is then about 3×10^{-4} for the experimental conditions employed.

Scission

Taylor and Tobolsky have suggested that cross-linking and scission reactions generally compete with each other in polymeric media when free radicals

are present (17). Although the insolubilization of the polymer shows that cross-linking is the predominant reaction taking place when potassium persulphate is added to GR-S latex, the possibility of a simultaneous degradative process should not be ignored.

Direct evidence on the rate of scission reactions, if present, is difficult to obtain with diene polymers because of the gelation caused by cross-linking. With vinyl polymers however, cross-linking does not seem to occur to any appreciable extent, and the rate of scission may be found from viscosity measurements. Accordingly, the effect of potassium persulphate on polystyrene latex was investigated.

For this purpose a polystyrene latex of 88% conversion was prepared by the bottle polymerization method (13). Residual styrene was removed by vacuum distillation at about 40° C. When treated with potassium persulphate, the polystyrene remained completely soluble but the viscosity molecular weight decreased slightly. Over a period of 41 hr. the intrinsic viscosity fell from 2.5 to 2.3.

By analogy with the quantitative treatment of cross-linking, the "scission rate constant" k_s may be defined by the equation:

$$\frac{d\left(\frac{1}{\bar{y}_n}\right)}{dt} = k_s c,$$

\bar{y}_n = number average degree of polymerization,

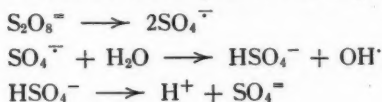
c = concentration of persulphate.

Values of \bar{y}_n were estimated from the intrinsic viscosity by means of the equation obtained by Goldberg, Hohenstein, and Mark (9). Calculation showed that for the same reaction conditions the scission rate constant, k_s , for polystyrene was less than 1% of the apparent cross-linking velocity constant, k_x , for GR-S. If the rate of scission with GR-S is of the same order of magnitude as with polystyrene it is evident that cross-linking is by far the dominant reaction at the temperature used.

Conclusions

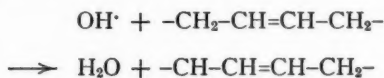
From an experimental viewpoint the use of potassium persulphate provides an attractively simple means of cross-linking diene polymer molecules. The reaction proceeds at a steady and easily controlled rate without seriously depleting the reaction source or contaminating the polymer with foreign materials.

A mechanism for the cross-linking may be inferred by analogy with the role of persulphates in the initiation of polymerizations. It appears likely that the first step in the process is thermal decomposition of the persulphate ion, viz.,

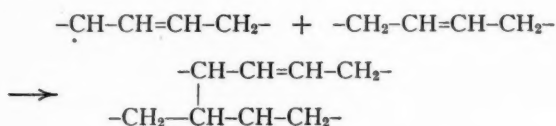


A plausible mechanism for the subsequent cross-linking would seem to be:

(1) Dehydrogenation at the α -methylene carbon of a polymerized butadiene unit:



(2) Addition of the free radical so formed to an unsaturated carbon of another polymerized butadiene unit:



Cross-linking may also occur when two such polymeric radicals combine.

Although the *initial* activation of the polymer probably occurs only at the polymer-water interface, the rapid loss of solubility suggests that the subsequent cross-linking takes place in a fairly uniform manner throughout the whole latex particle. The tendency for random cross-linking is favored by the minute dimensions of latex particles and the possibility of frequent chain transfer of the active center prior to the actual inter-linking step.

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THE FORMATION AND PROPERTIES OF THREE-DIMENSIONAL POLYMERS

III. THE EFFECT OF NETWORK STRUCTURE ON ELASTIC PROPERTIES¹

J. BARDWELL² AND C. A. WINKLER

Abstract

The tension exerted by stretched rubber at a given temperature and elongation is determined by the initial molecular weight and the concentration of cross-linkages. With the copolymer of butadiene and styrene (GR-S), the effect of molecular weight on elastic properties is identical with that found by Flory for butyl rubber and arises from the inactivity of terminal chains. When the molecular weight is fixed, the retractive force is approximately linear with the degree of cross-linking, in agreement with the statistical mechanics of rubber elasticity.

Introduction

In a previous paper of this series theoretical treatments of the elastic behavior of three-dimensional polymers were reviewed (1). It is the purpose of the present paper to compare the theoretical predictions with the observed behavior of networks formed from the copolymer of butadiene and styrene (GR-S).

Experimental

Preparation of Polymers

The GR-S polymers were prepared in emulsion by the well known bottle polymerization method (21, 26). The following recipe was employed.

Water	180 parts
Butadiene	75 "
Styrene	25 "
Soap	5 "
Potassium persulphate (Merck's reagent grade)	0.3 "
Tertiary dodecyl mercaptan (Sharples 3-B)	Variable

By varying the amount of mercaptan used a wide range of molecular weight was obtained. The number average degree of polymerization, \bar{y}_n , and the heterogeneity index, $\frac{\bar{y}_w}{\bar{y}_n}$, of the primary molecules were calculated by means of equations given previously (1, Equations 13 and 14). The "regulating index" of tertiary dodecyl mercaptan is 3.16 (26). In computing chain lengths due allowance was made for compositional changes during polymerization (24). Relevant characteristics of the polymers are given in Table I.

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TABLE I

DEGREE OF POLYMERIZATION AND HETEROGENEITY INDEX OF MODIFIED GR-S POLYMERS

Polymer No.	Mercaptan charged (moles per mole of initial monomer), R_0	Conversion α	Number average degree of polymerization \bar{y}_n	Heterogeneity index $\frac{\bar{y}_w}{\bar{y}_n}$
I	0.44	0.304	11600	2.16
II	1.42	0.232	3150	2.09
III	2.95	0.465	2080	2.38
IV	4.47	0.107	870	2.02
V	4.47	0.275	1100	2.13
VI	4.47	0.356	1220	2.22
VII	7.37	0.171	575	2.05
VIII	14.2	0.136	275	2.03
IX	58.9	0.515	110	2.52

Cross-linking Reaction

After the addition of a small amount of hydroquinone to prevent further polymerization, residual monomer was removed from the emulsion by vacuum distillation at about 40° C. A buffered solution of potassium persulphate was then added to promote cross-linking (2).

To compare this cross-linking reaction with more conventional vulcanizations, one of the polymers (VI) was mixed with compounding ingredients and cured at 140° C. The curing ingredients were added as a colloidal dispersion to the latex, which was then coagulated in butanol. The composition of the coagulum was approximately as follows:

Polymer	100 parts
Sulphur	2 "
Benzthiazyl disulphide	2 "
Phenyl- β -naphthylamine	2 "
Zinc oxide	1 "

After a short period of milling at room temperature to obtain thorough mixing, portions of the coagulum were cured at 140° C.

Solubility and Swelling

The gel fraction and swelling volume of the cross-linked polymers were determined by the static extraction method (2).

Modulus

Stress-strain curves were determined for several GR-S pure gum vulcanizates by means of a standard testing machine. The rate of extension was 20 in. per min. In addition to the "dynamic" modulus obtained in this way, the "static" modulus was estimated by subtracting the stress-relaxation that took place when a test specimen was held at a relative elongation of 300% for 24 hr.

Results and Discussion

The Relation of Swelling to Modulus

In a previous paper (1) it was pointed out that several theoretical treatments of the phenomenon of rubberlike elasticity lead to an "equation of state" of the form:

$$\tau = \frac{\nu}{V} RT \left(\frac{l}{l_0} - \frac{l_0^2}{l^2} \right) \quad (1)$$

τ = tension (force per unit area of initial cross section),

R = gas constant,

T = absolute temperature,

l = stretched length,

l_0 = unstretched length.

Several authors (11, 30, 31) have interpreted ν as the number of "chains" in volume V , but here it is convenient to consider the ratio $\frac{\nu}{V}$ as the "network activity", i.e., as an *experimental* quantity defined by Equation (1). Here, it is the dependence of $\frac{\nu}{V}$ on network structure that is of main concern.

Consideration of the phenomenon of swelling as a three-dimensional stretching (12) results in a relation between equilibrium swelling volume and "network activity" $\frac{\nu}{V}$:

$$\frac{\nu}{V} = \frac{\ln(1 - v_2) + v_2 + \mu_g v_2^2}{-V_1 v_2^{1/3}} \quad (2)$$

v_2 = reciprocal of the equilibrium swelling volume,

μ_g = solvent-polymer interaction coefficient (7, 18),

V_1 = molar volume of solvent.

By expanding the term $\ln(1 - v_2)$ and combining the resulting expression with Equation (1), it is found that the "modulus" (tension at a given elongation) of the unswollen rubber is predicted to be approximately inversely proportional to the 5/3 power of the equilibrium swelling volume.

Measurements of modulus and swelling with GR-S pure gum vulcanizates amply confirm this relation. Fig. 1 consists of a log-log plot of the "dynamic" and "static" moduli at 300% elongation (τ_{300}) vs. the equilibrium swelling volume in toluene ($S.V.$). Although both dynamic and static moduli show good correlation with the swelling volume, better agreement with theory is found for the static modulus. This result is not surprising, since swelling represents an equilibrium type of deformation.

The equation of the line in Fig. 1 for the static modulus is

$$\log \tau_{300} = 3.67 - 1.67 \log S.V.$$

The theoretical slope of $(-5/3)$ is found and the Flory-Rehner treatment of swelling thereby substantiated (12). By comparing the above results with Equations (1) and (2) the value of μ_g for GR-S in toluene is found to be 0.18.

Small variations of styrene content of the polymer do not appear to alter this value significantly (Fig. 1).

The observed correlation between modulus and equilibrium swelling volume agrees with results obtained with butyl rubber (6, 8), and provides further

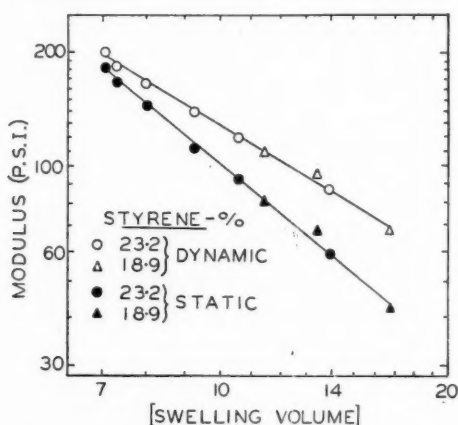


FIG. 1. Modulus at 300% elongation vs. swelling volume (log-log plot).

evidence that the elastic reaction in both deformation processes is governed by the same structural factors. The "network activity" may therefore be estimated from either measurement.

The Coefficient μ_0

Since the thermodynamic properties of polymer solutions and gels are still under active discussion (3, 15), it seems worthwhile to consider briefly values of the coefficient μ_0 as estimated from the swelling-modulus correlation. Table II shows the measured values of the equilibrium swelling volume of a GR-S gel in various organic solvents, together with values of μ_0 calculated by means of Equation (2).

TABLE II
SWELLING CHARACTERISTICS OF GR-S IN VARIOUS LIQUIDS

Liquid	Equilibrium swelling volume	μ_0	Cohesive energy density, E_1 , cal./cc.
Ethyl ether	9.3	0.47	58
Methyl amyl ketone	11.3	0.40	61
Carbon tetrachloride	23.1	0.21	73
Xylene	22.4	0.14	77
Toluene	23.0	0.18	80
Benzene	22.0	0.26	84
Chloroform	25.9	0.20	86
Chlorobenzene	22.5	0.20	91
Nitrobenzene	9.3	0.47	99

In theory (7, 18) the quantity μ_θ is related to the heat of mixing of solvent and polymer by the equation

$$\mu_\theta = \frac{1}{Z} + \frac{\Delta\bar{H}_1}{RT v_2^2}, \quad (3)$$

Z = co-ordination number of the lattice model (7, 18),

$\Delta\bar{H}_1$ = partial molal heat of mixing,

v_2 = reciprocal swelling volume.

An approximate estimate of the partial molal heat of mixing may be made by means of the Scatchard expression (27)

$$\Delta\bar{H}_1 = V_1 v_2^2 (\sqrt{E_1} - \sqrt{E_2})^2 \quad (3')$$

E_1 and E_2 are the cohesive energy densities of solvent and polymer respectively.

Equations (3) and (3') suggest that μ_θ should pass through a minimum when $E_1 = E_2$. Cohesive energy densities for several liquids have been estimated by Gee (14, p. 183) and by Scott *et al.* (28) from heats of evaporation and are included in Table II. There appears to be a minimum in the value of μ_θ when E_1 is about 77 but chloroform and chlorobenzene are somewhat out of line, possibly because of their polar nature.

In comparing values of μ_θ estimated from the swelling-modulus correlation with those obtained by other methods, it is to be noted that the value of 0.26 for GR-S in benzene is less than the value of 0.36 found by French and Ewart from measurements of the osmotic pressure of dilute solutions of GR-S in benzene (13). A similar observation with butyl rubber (8) has been attributed to failure of the elementary statistical theory in the region of dilute solutions (7). If the lowest value of μ_θ (0.14 for xylene) is taken to correspond to zero heat of mixing, the co-ordination number Z appears to have an experimental value of about seven.

Swelling and Network Structure

In considering the effect of network structure on equilibrium swelling volume it is convenient to interpret the measured swelling in terms of the retractive force that the network exerts against the swelling pressure of the solvent.

The "network activity", $\frac{v}{V}$, which appears in Equations (1) and (2) will be employed for this purpose.

The network structure, on the other hand, is determined by the concentration of cross-linkages and the molecular weight distribution prior to cross-linking (1, 6). If all the molecules are bound to the network the theoretical dependence of network activity, $\frac{v}{V}$, on these structural factors is given by:

$$\frac{v}{V} = g \frac{d}{M_0} \left(\rho - \frac{2}{\bar{y}_n} \right), \quad (4)$$

- d = density of polymer,
 M_0 = molecular weight of the structural unit (monomer),
 ρ = fraction of structural units involved in cross-linkages,
 \bar{y}_n = number average degree of polymerization prior to cross-linking,
 g = a proportionality "constant" which has a theoretical value of unity in the Wall-Treloar-Flory-Rehner treatments of the elasticity problem (11, 30, 31). In the theory of Kuhn (22, 23), g has the value $7/3$ and in that of James and Guth (20) about $1/2$.

Equation (4), which presents an explicit connection between the "modulus" of vulcanized rubber and its network structure, has hitherto received only partial experimental verification. Flory (6, 8) has shown that the elastic properties of butyl vulcanizates of a fixed degree of cure (ρ constant) depend on primary molecular weight as indicated in Equation (4). The predicted effect of cross-linking has however received little direct support, and several alternative analyses of the phenomenon of elasticity have recently been proposed (17, 19, 25).

The determination of the primary molecular weight as required for experimental testing of Equation (4) presents no great difficulty if the polymerization kinetics are sufficiently understood. For example when a chain transfer agent (modifier) is present during chain growth, the primary molecular weight distribution may be calculated from modifier consumption (1).

The degree of cross-linking, ρ , is however a more elusive quantity and its determination requires closer examination of the process of network formation. In a previous paper (2) a method of cross-linking polymer molecules by the addition of potassium persulphate to a latex was described. It was shown that the conversion to gel in this process is in good agreement with the predictions of the statistical theory of random cross-linking. The measured gel fraction may therefore be interpreted as reflecting the presence of a definite concentration of cross-linkages in the polymer. Specifically, if the primary molecular weight distribution is known and the gel fraction has been measured, the degree of cross-linking of the polymer may be estimated with the assistance of suitable statistical relations (1, Fig. 2).

This principle was applied to the gels obtained by cross-linking the polymers listed in Table I. The degree of cross-linking, ρ , was calculated from the measured gel fraction, the heterogeneity index being employed for the necessary interpolations (1). The "network activity" $\frac{p}{V}$ was computed from the swelling volume by means of Equation (2) with the value of 0.18 for μ_0 .

Fig. 2 shows the effect of both primary chain length and degree of cross-linking on the "network activity" (modulus) of GR-S. The influence of primary molecular weight is particularly noteworthy. Polymers of low primary chain length are handicapped in the development of reversible elasticity since relatively large concentrations of cross-linkages are required for the formation of a network. Even after the "gel point" is reached, the

increase of modulus is less rapid than with polymers of high primary molecular weight, since a greater fraction of the additional cross-linkages are "wasted" in attaching new material to the network.

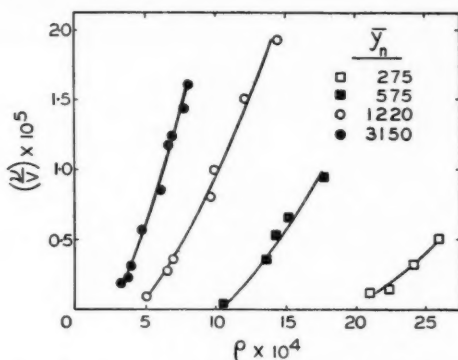


FIG. 2. Network activity vs. degree of cross-linking.

Before employing the results shown in Fig. 2 to test Equation (4), it should be noted that this Equation is intended only for completely insoluble polymers. When an appreciable fraction of extractable sol exists, only the structure of the gel is of interest. Equation (4) should then be modified to

$$\frac{\bar{\nu}}{\bar{V}} = g \frac{d}{M_0} \left(\rho'' - \frac{2}{\bar{y}_n} \right), \quad (5)$$

ρ'' and \bar{y}_n are the values of ρ and \bar{y}_n in the gel.

To determine the "effective" degree of cross-linking $\left(\rho'' - \frac{2}{\bar{y}_n} \right)$ it is necessary to consider the partition of cross-linkages and of primary molecules between sol and gel (9). Details of the required calculations and the results for various initial distributions were given previously (1). A plot of $\frac{\bar{\nu}}{\bar{V}}$ vs. $\rho'' - \frac{2}{\bar{y}_n}$ then allows direct testing of the theoretical dependence of elastic modulus on network structure.

Fig. 3 shows that all the experimental results are in satisfactory agreement with Equation (5). The effect of molecular weight over a hundredfold range is therefore accounted for quantitatively by the postulate that terminal chains are inactive during deformation. The linearity of the resulting plot also verifies the proportionality between network activity and (effective) degree of cross-linking predicted by statistical mechanical treatments of rubber elasticity. The equation of the line in Fig. 3 is:

$$\frac{\bar{\nu}}{\bar{V}} = 0.039 \left(\rho'' - \frac{2}{\bar{y}_n} \right).$$

Substituting $d = 0.93$
 $M_0 = 59.2$

in Equation (5), the value of g is found to be 2.5, in good agreement with the value of $7/3$ predicted by Kuhn.

Fig. 3 includes results deduced from the swelling and solubility of GR-S pure gum vulcanizates at low degrees of cure. The above conclusions concerning the effect of network structure on elastic properties appear to be equally applicable to GR-S vulcanizates.

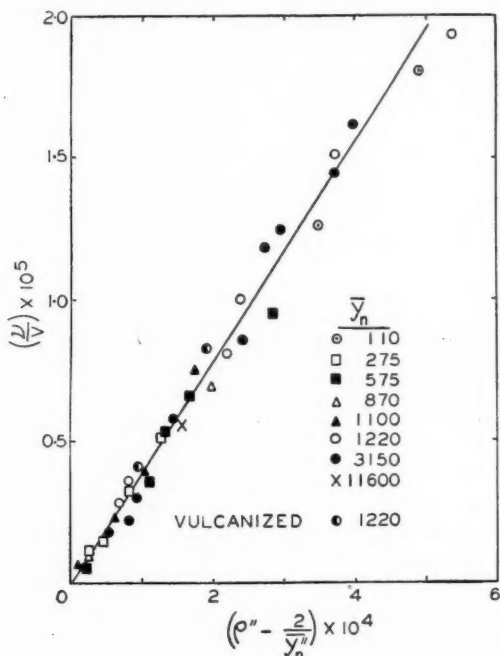


FIG. 3. Network activity vs. effective degree of cross-linking.

The effect of much higher concentrations of cross-linkages was investigated by extending the reaction period with one of the polymers (III). The degree of cross-linking of the resulting essentially insoluble polymers was calculated from the measured rate of insolubilization early in the reaction, due allowance being made for changes of persulphate concentration (2).

The results, shown in Fig. 4, indicate that here the modulus increases more rapidly than the effective degree of cross-linking. In this respect the results for GR-S appear to differ from those obtained by Flory (6) with butyl rubber ($g = 3.3$ and 2.1), also shown in Fig. 4 together with the predictions of several elasticity theories. Of the various theories, that of Kuhn appears to be in best agreement with the experimental results for GR-S except at relatively high concentrations of cross-linkages. The hypothesis of Kuhn (23) and of

Flory (6) that other restraints in addition to chemical cross-linkages exist along the chains appears to be qualitatively correct.

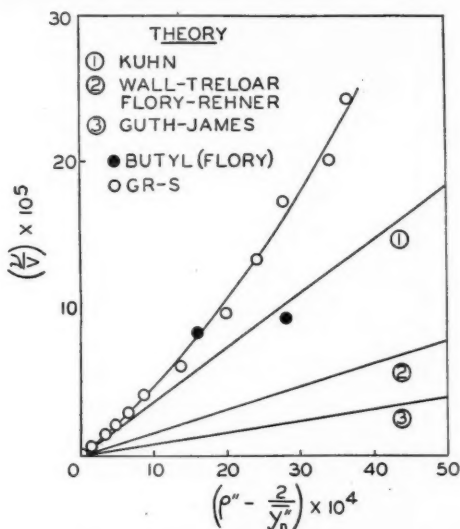


FIG. 4. Network activity vs. effective degree of cross-linking. Comparison of experimental results for GR-S and for butyl rubber (Flory) with elasticity theories.

Estimation of Primary Molecular Weight

The simple dependence of swelling volume on network structure discussed above may be exploited to reveal the molecular weight of the polymer from which a gel was formed. Rearranging Equation (5) gives:

$$\bar{M}_n = \frac{gd \left\{ \bar{y}_n \left(\rho'' - \frac{2}{\bar{y}_n''} \right) \right\}}{\frac{\nu}{V}}$$

\bar{M}_n = number average primary molecular weight.

The term in parentheses in the numerator of this expression may be calculated from the solubility (1, Fig. 4) and the denominator from the swelling volume [Equation (2)]. Use of the empirical value of about 2.5 for g then permits estimation of the primary molecular weight, i.e., the molecular weight in the entire absence of cross-linkages. A few examples of the use of this novel method will be given.

(1) *Commercial GR-S*.—A GR-S latex of 70% conversion modified by commercial dodecyl mercaptan was treated with potassium persulphate (2), and the solubility and swelling of the resulting gels interpreted as in the preceding section. [The form of the primary distribution to be expected in such a polymer corresponds to about 90% modifier depletion (16)]. In

Fig. 5, $\frac{\nu}{\bar{V}}$ is plotted vs. $\bar{y}_n \left(\rho'' - \frac{2}{\bar{y}_n} \right)$. The slope of the resulting line is 4.7×10^{-5} from which \bar{M}_n , the primary molecular weight, may be estimated at about 50,000.

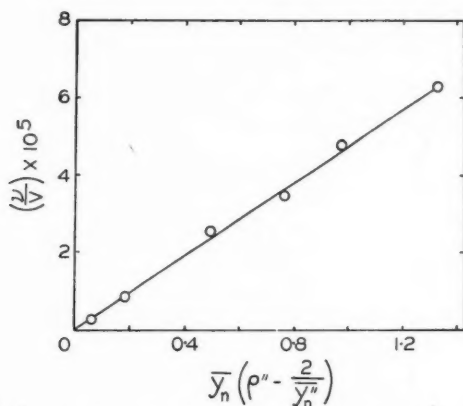


FIG. 5. Network activity vs. number of effective chains per primary molecule.

(2) *Natural Rubber*.—Since rubber in the native state generally contains a gel fraction, its *primary* molecular weight prior to degradation may be estimated roughly by the method under discussion. For this purpose it was assumed that the network structure of natural rubber and of GR-S are similar, i.e., a value of 2.5 was used for g . The coefficient μ_0 for natural rubber in benzene was estimated at about 0.33. Measurements of the solubility and swelling of dried films of natural rubber yielded values of the order of 300,000 for the primary molecular weight.

(3) *Heat-softened GR-S*.—The gel fraction of essentially insoluble (unmodified) GR-S or Buna-S may be substantially reduced by heating in air or oxygen. An experimental study of such reactions was made in this laboratory by Dr. T. A. Eastwood (5). Oxygen at 100° C. was passed over the finely divided polymer and the changes of gel fraction and swelling index measured. (The swelling index is defined as the *weight* ratio of swollen to dried gel.) Typical results are shown in Fig. 6. It is seen that the gel fraction falls initially, but rises as the treatment is prolonged. Similar trends have been observed by Cole and Field (4).

From these results the primary chain length, \bar{y}_n and the degree of cross-linking, ρ , were calculated. In Fig. 6 the reaction is resolved into its cross-linking and scission components by plotting ρ and $\frac{1}{\bar{y}_n}$ against time of reaction. This analysis suggests that both scission and cross-linking are proceeding at comparable rates. During the initial part of the reaction, scission is slightly

avored, but is subsequently overtaken by the cross-linking process. On this basis there is no reason to believe that heat-softening proceeds through specific attack by oxygen at the chemical cross-linkages.

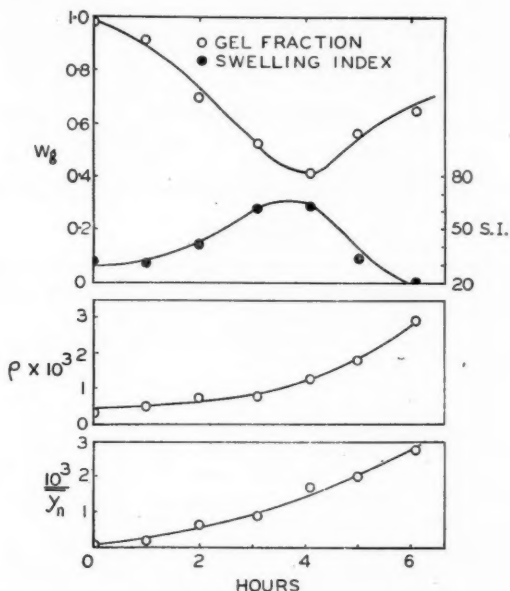


FIG. 6. Relative rates of cross-linking and scission during heat-softening.

Conclusions

In the correlation between elastic properties and network structure it is the influence of molecular weight that is of greatest practical importance. This effect stems from the fact that each end of a primary molecule results in a "flaw" which impairs the properties of the final network (8, 10). The low value of the primary molecular weight of GR-S as now produced indicates that such "flaws" may be quite prevalent in its vulcanizates.

It is to be noted that for satisfactory correlation of elastic properties with molecular weight it is the *primary* rather than the actual molecular weight that should be considered. When cross-linking reactions accompany chain growth the resulting polymer contains "clusters" of molecules which severely distort the *actual* molecular weight distribution. The weight average molecular weight is greatly affected by the presence of such clusters (9, 29). Their influence is revealed by empirical expressions for the viscosity molecular weight (16) which show that in the neighborhood of the gel point only a small fraction of the viscosity is due to the lengths of the *primary* molecules. For this reason good correlation of elastic properties with viscosity molecular weight can scarcely be expected.

The effect of *distribution* of primary molecular weight on elastic properties may be discussed in terms of the increase in number of effective chains during cure (1, Fig. 3). For a given number average primary chain length a fixed degree of cross-linking leads to a slightly greater fraction of effective chains with the more *heterogeneous* polymer. In practice however this advantage of heterogeneity may be offset to some extent by the increased difficulties of processing.

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